

## MEMORANDUM OF UNDERSTANDING ( MoU)

This Memorandum of Understanding is made on the 31<sup>st</sup> day of March 2016 and it is valid up to 30th March 2026 (10 Years)

### BETWEEN

**Luminescence Laboratory, Department of Physics, Rashtrasant Tukadoji Maharaj, Nagpur University Nagpur (First Party)**  
**AND**

**Principal & Department of Chemistry, Sevadal Mahila Mahavidyalaya, Sakardara Square, Umrer Road, Nagpur (Second Party)**

### BACKGROUND

- A. Each of the Party owns and operates facilities for the provision of
1. Laboratories use
  2. Students exchange for Research.
  3. Use and Exchange of Research activities.
  4. Collaborative Research Publication.
  5. Patent Publications.
- B. The Party currently have an arrangement with each other with respect to the training, borrowing, and Awareness of Knowledge material that each Member Council works together with resource sharing, Knowledge sharing and maintenance of a shared resources.
- C. Each of the Party agrees that the MOU shall be collectively known as **"To Exchange of Research activities and Collaborative Research Publications"**.
- D. The Party desire to formalise their agreement and understanding in relation to the Network and have agreed to enter into this Memorandum of Understanding in this regard. However, the Party agree that this Memorandum shall not create any legal obligations and whilst recognising that there are no enforceable obligations between them the Party agree to perform their obligations pursuant to this Memorandum in good faith and to the best of their abilities.
- E. The Party agree that each of them shall have the following obligations in respect of **"To Demonstrate and Hands-on training of Laboratory equipment"**.
- F. **Second Party (Administer)**

On behalf of the Other Member Councils, the Second party agrees;



**Principal**

Sevadal Mahila Mahavidyalaya  
Umrer Road, Nagpur-9.

## AND THE PARTIES AGREE:

### 1.1 Interpretation

- 1.1.1 The Background set out above forms part of this Memorandum and the Party agree that the Background is true and accurate.
- 1.1.2 Unless the contrary intention appears:
  - 1.1.2.1 Words noting the singular shall include the plural and vice versa.
  - 1.1.2.2 Reference to any gender shall include every other gender and words denoting individuals shall include corporations and vice versa.
  - 1.1.2.3 Reference to any Act of Parliament, statute or regulation shall include any amendment currently enforce at the relevant time and any Act of Parliament, statute or regulation enacted or passed in substitution therefore.
  - 1.1.2.4 Headings are for convenience of reference only and do not affect the interpretation or construction of this Memorandum.
  - 1.1.2.5 A requirement in this Memorandum for liaison and consultation is a requirement for full and frank discussion and includes a requirement where necessary and appropriate, for full disclosure of relevant information and material.

### 2. Term

- 2.1 The term of this Memorandum shall be of ten (10) years commencing on 31//03/2016 and expiring on the 30/03/2026, unless otherwise agreed or extended by the Party in writing.
- 2.2 The term shall be reviewed by the Party not more than twelve (12) months and not less than six (6) months prior to the expiration of the term subject to the term being reviewed prior to this period.

### 3. Negotiate In Good Faith

The Party agree that they will cooperate with each other and at all times act in good faith and with the joint objective of successfully and expeditiously concluding and carrying out all of the arrangements and agreements contemplated in this Memorandum.

### 4. The Party Obligations

#### 4.1.1 Administration

- 4.1.1.1 to administer the work in accordance with this Memorandum and the Operating Guidelines; and
- 4.1.1.2 to be accountable to the Other Party in a manner determined for the administration of the MOU and the facilitation of the MOU;

#### 4.1.2 Finances

- 4.1.2.1 Network Costs and the Administration Cost is mandatory to administer (Second Party)



  
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4.1.2.2 to prepare with the assistance from the Other Member Councils, in accordance with this Memorandum, the budgets for the Network; and

4.1.2.3 to meet all auditing requirements for all monies received and paid for in relation to the Network;

**4.1.3 Membership of the Committee**

4.1.3.1 the Chief Executive Officer or delegated officer is a Principal and the nominee to the Committee is a Concern Department Head;

4.1.3.2 to appoint a representative (Should be a Faculty of Concern Department) from each party;

**4.2 All Member Councils**

The Party agree:

**4.2.1 Reporting**

To consider reports and recommendations from its respective representatives on the Committee in relation to the administration of the MOU.

4.2.2 The Committee shall at its first meeting (and annually thereafter) appoint amongst the representatives a Chairperson who shall hold office for a term of one (1) year but is eligible for reappointment for a further term, unless he/she resigns in which case the Committee shall appoint a new Chairperson to chair the meetings.

4.2.3 In the event that the appointed Chairperson is absent from a Committee meeting the representatives present shall appoint an acting Chairperson, who shall preside over that meeting or until the Chairperson is present.

**5. Operational Guidelines**

5.1 Upon execution of this Memorandum, the Chief Executive Officer or delegate of each of the Party shall prepare and implement Operational Guidelines which the Chief Executive Officers or delegates shall be capable of amending from time to time as the Chief Executive Officers or delegates see fit.

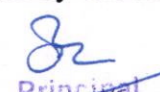
5.2 Notwithstanding the provisions of this Memorandum, the Party agree that the Operational Guidelines shall be the operative document that facilitates the operational management of the MOU.

5.3 The Party shall delegate to their respective Chief Executive Officers such powers as are required and necessary to prepare and amend the Operational Guidelines and to manage the network in accordance with the Operational Guidelines.

5.4 The Parties agree to negotiate and cooperate with each other at all times and to act in good faith in the operation of the Operational Guidelines and to comply with its terms.

The Parties agree that the terms and conditions of this Memorandum may be varied upon written agreement of the proposed variation by **all** the Member Councils.



  
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6. **Liability**




6.1 The **Second Party** shall indemnify and keep indemnified the other Party against all actions, costs, claims, damages, charges in respect of injury, loss or damage resulting from any negligent act or omission of The **First Party Council**;

7. **Acknowledgement**

The Party acknowledge and agree that each of the Party may in its own right engage the other Member Council staff for their services; however any agreed costs incurred by the Council in doing so shall be borne solely by the respective Party.

**EXECUTED** as a Memorandum of Understanding

<p><b>THE SEAL of THE First Party COUNCIL</b> was hereunto affixed in accordance with its Constitution and by the authority of its directors:</p> <p>Name: <b>Dr. Sanjay J. Dhoble</b>,  <b>Professor, Luminescence Laboratory, Department of Physics, R.T.M. Nagpur University, Nagpur</b></p>	<p>Sign &amp; Seal</p>  <p><b>Dr. S. J. Dhoble</b>  <b>Professor</b>  <b>Department of Physics</b>  <b>RTM Nagpur University</b>  <b>Nagpur</b></p>
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<p><b>THE SEAL of the Second Party COUNCIL</b> was hereunto affixed in accordance with its Constitution and by the authority of its directors:</p> <p>Name: <b>Prof. Pravin Charde</b>  Principal</p>	<p>Sign &amp; Seal</p>   <p><b>Principal</b>  <b>Sevalal Mahila Mahavidyalaya,</b>  <b>Umrer Road, Nagpur-9</b></p>
<p>Name: <b>Dr. (Mrs) N. S. Dhoble</b>  .....  Professor, Department of Chemistry</p>	<p> <b>Dr. (Mrs.) N. S. Dhoble</b>  <b>Professor, Chemistry, Department</b>  <b>Sevalal Mahila, Mahavidyalaya</b></p>

\*\*\*\*\*



  
**Principal**  
**Sevalal Mahila Mahavidyalaya**  
**Umrer Road, Nagpur-9.**





## Full Length Article

Photo and thermoluminescence in  $K_2Mg(SO_4)_2$ : Dy phosphor and evaluation of trapping parametersArchana Deshpande<sup>a</sup>, N.S. Dhoble<sup>b</sup>, S.C. Gedam<sup>c,\*</sup>, S.J. Dhoble<sup>a</sup><sup>a</sup> Department of Physics R.T.M. Nagpur University, Nagpur 440033, India<sup>b</sup> Department of Chemistry, Sevadal Mahila Mahavidyalaya, Nagpur 440017, India<sup>c</sup> Department of Physics, K. Z. S. Science College, Kalmeshwar, Nagpur 441501, India

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Phosphor

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 $\gamma$ -radiation

XRD

Rare earth

## ABSTRACT

The prepared phosphor  $K_2Mg(SO_4)_2$ :Dy is synthesized by solid state diffusion (SSD) method. The sample was studied for its photoluminescence (PL) and thermoluminescence (TL) characteristics. In the emission spectra of  $K_2Mg(SO_4)_2$ :Dy excited by 350 nm UV light, the emission line at 576 nm ( $^4F_{9/2}$ – $^6H_{13/2}$ ) and 487 nm ( $^4F_{9/2}$ – $^6H_{15/2}$ ) from the  $Dy^{3+}$  ions coexist with the wide emission band from the  $K_2Mg(SO_4)_2$  host. The excitation spectra of the emission at 576 nm consist mainly of the strong excitation band of the  $K_2Mg(SO_4)_2$  host at 350 nm. TL characteristics show excellent results by the same SSD method. The samples were irradiated by  $\gamma$ -radiation for 5–30 Gy from  $^{60}Co$  source at the dose rate of  $0.322\text{ kGy h}^{-1}$ . The TL glow curve shows the simple structure having the peak temperature nearly at  $185^\circ\text{C}$ . The single peak is due to the possibility of formation of only one kind of trapping site due to  $\gamma$ -irradiation. The effect of concentrations of Dy and  $\gamma$ -radiation doses does not change the general structure of the TL glow curve but the intensity is found to be increased as per the higher concentrations and dose. The trapping parameters are also evaluated by Chen's method. The values of trap depth ( $E$ ) and frequency factor ( $s$ ) were found to be  $0.77 \pm 0.002\text{ eV}$  and  $3.5 \times 10^8\text{ s}^{-1}$  respectively. The study of PL, TL and evaluation of trapping parameters has been done and discussed for first time.

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## 1. Introduction

Sulfates are used as a promising material for the photoluminescence (PL) and thermoluminescence (TL) phosphors due to their noticeable characteristics [1]. Keeping this in mind, a choice of Dy doped  $K_2Mg(SO_4)_2$  were carefully considered after many trials for the purpose of obtaining a good PL and TL of such systems to be used for luminescence applications. In recent years Moharil and co-workers have reported several phosphors on rare earth (RE) ions doped mixed sulfate [2–8]. Also some work has been done by Sahare and et al. in some mixed sulfates [9–15]. Moreover sulfates are known to be good candidate as luminescent material due to the fact that they possess well desired characteristics like high-temperature glow peak, linear response with ionizing radiation exposure, low fading and an easy method of preparation [16]. Recently, site selective luminescence of  $Eu^{3+}$  ions in  $K_2Mg(SO_4)_2 \cdot 6H_2O$  crystal has been studied by Marzougui et al. [17].

The main goal of measuring and analyzing TL glow curves is the extraction of several parameters that can be used to describe the

TL process in the material. The dosimetric characteristic of any TL phosphor mainly depends on its trapping parameters which describe the defect centers responsible for the TL emission, hence it was tried to calculate in  $K_2Mg(SO_4)_2$ : Dy material. The positions, shapes and intensities of the glow peaks are related to the various parameters of the trapping states responsible for the TL. The trapping centers responsible for the thermoluminescence (TL) were quantitatively described by the various kinetic parameters such as activation energy, frequency factor and order of kinetics in  $K_2Mg(SO_4)_2$ : Dy. Various experimental techniques such as curve fitting methods, Chen's half width methods, heating rate methods, isothermal decay analysis methods, etc., have been developed to determine these parameters from TL glow curves. Here we have used Chen's half width method for the calculations. The aim of present study is to study of its PL and TL characteristics for different dose rates and calculation of kinetic parameters.

## 2. Experimental

The present phosphor  $K_2Mg(SO_4)_2$  doped with Dy has been synthesized by solid state diffusion method. For the preparation of the samples, the rare earth material (Dysprosium) has been taken

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RESEARCH ARTICLE

# Luminescence characterization of Dy and Eu doped $\text{Na}_6\text{Mg}(\text{SO}_4)_4$ phosphors

Bhushan P. Kore<sup>1,3\*</sup> | Shilpa A. Pardhi<sup>1</sup> | N. S. Dhoble<sup>2</sup> | S. J. Dhoble<sup>1</sup> | H. C. Swart<sup>3</sup>

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## Abstract

A series of single-phase phosphors based on  $\text{Na}_6\text{Mg}(\text{SO}_4)_4$  ( $Z_{\text{eff}} = 11.70$ ) doped with Dy and Eu was prepared by the wet chemical method. The photoluminescence (PL) and thermoluminescence (TL) properties of  $\text{Dy}^{3+}$ - and  $\text{Eu}^{3+}$ -activated  $\text{Na}_6\text{Mg}(\text{SO}_4)_4$  phosphors were investigated. The characteristic emissions of  $\text{Dy}^{3+}$  and  $\text{Eu}^{3+}$  were observed in the  $\text{Na}_6\text{Mg}(\text{SO}_4)_4$  host. The TL glow curve of the  $\text{Na}_6\text{Mg}(\text{SO}_4)_4:\text{Dy}$  phosphor consisted of a prominent peak at 234°C and a very small hump at 158°C. The TL sensitivity of the  $\text{Na}_6\text{Mg}(\text{SO}_4)_4:\text{Dy}$  phosphor was found to be four times less than the commercialized  $\text{CaSO}_4:\text{Dy}$  phosphor. The TL dose-response of the  $\text{Na}_6\text{Mg}(\text{SO}_4)_4:\text{Dy}$  phosphor was studied from a dose range of 5–10 kGy and the linear dose-response was observed up to 1 kGy which is good for a microcrystalline phosphor. Trapping parameters for both the samples were calculated using the Initial Rise and Chen's peak shape methods.

## KEYWORDS

phosphor, thermoluminescence, trapping parameters, wet chemical method

## 1 | INTRODUCTION

In an imperfect insulator various defects are present that cause localized states in forbidden band gaps. Thermoluminescence (TL) is usually observed in insulating crystals that have been previously exposed to ionizing radiation when they are heated above room temperature. Irradiating the material using ionizing radiation creates electron-hole pairs inside the host material. These free moving electrons and/or holes get trapped at localized states, the localized levels may be defect centres or vacancies.<sup>[1]</sup> The trapped charges (either electrons or holes) are inefficient in their ability to liberate the electrons out of the trap at room temperature. When irradiated material is heated to sufficiently higher temperatures, the trapped charges are liberated out of the trap at a particular temperature and recombine with their counterpart particles.<sup>[2]</sup> The recombination results in emission of light, the so-called 'thermoluminescence'. Trapping of charge carriers and light emission is directly proportional to the irradiation dose given to the sample. The greater the dose the more will be the trapping, which leads to increase in recombination probability and hence the emission of large numbers of photons. This property of the material is useful in dose determination of ionizing radiation within the region, where the response related to the dose given to material and photons generated is linear.<sup>[1,2]</sup>

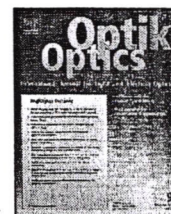
Abbreviations: AR, analytical reagent; CGCD, Computerized Glow Curve Deconvolution; GCD, Glow Curve Deconvolution; IR, infra-red; TLD, thermoluminescent dosimetry; XRD, X-ray powder diffraction.

Among the relative dosimetry techniques, thermoluminescence dosimetry (TLD) has gained widespread use because of its simplicity, excellent spatial resolution and the ability to integrate the absorbed dose over extended periods of time. TL is a very popular and simple technique used for dosimetry of ionizing radiation. The intensity of light emitted by a phosphor is proportional to the irradiation doses given to it and, by calibration with known doses of high-energy radiation, unknown doses could also be estimated when several other parameters such as energy dependence, fading, post-irradiation effect etc. are taken into consideration. The main application of these TLDs is in personnel dosimetry and studies of photon and electron beam dose distribution in phantoms. Seldom TLDs used in direct surface or intracavitary dose measurement in the patient.<sup>[3–7]</sup>

Rare earth (RE)-doped crystalline solids are known to be interesting TL materials that can be used for radiation dosimetry. Particularly  $\text{Tm}$  and  $\text{Dy}$  doped  $\text{CaSO}_4$  show a high sensitivity over a wide range of radiation frequencies ranging from  $\gamma$ -rays to ultraviolet (UV) radiation.<sup>[8–12]</sup> Since, the development of  $\text{CaSO}_4$  doped with different rare earths as described by Yamashita et al., this approach has taken a significant lead in personal and environmental radiation monitoring using TL dosimetry and with these materials as sensing elements.<sup>[13]</sup>  $\text{CaSO}_4:\text{Dy}$  (TLD-900) is one of the high sensitive sulphate-based TLD







## Original research article

Novel RGB emission of  $\text{Tb}^{3+}$  ion in  $\text{Li}_2\text{BaP}_2\text{O}_7$  phosphor for near-UV LEDsJ.A. Wani<sup>a</sup>, N.S. Dhoble<sup>b</sup>, S.J. Dhoble<sup>a,\*</sup><sup>a</sup> Department of Physics, R.T.M. Nagpur University, Nagpur, 440033, India<sup>b</sup> Department of Chemistry, Sevadal Mahila Mahavidyalaya, Nagpur, 440009, India

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 $\text{Li}_2\text{BaP}_2\text{O}_7:\text{Tb}^{3+}$ 

Red emission

Phosphor

Lamp phosphor

## ABSTRACT

A red emitting  $\text{Li}_2\text{BaP}_2\text{O}_7:\text{Tb}^{3+}$  phosphor prepared through solid state reaction method is first time reported in this work. The main point of this work is that  $\text{Tb}^{3+}$  shows intense red line in addition to blue and green lines in  $\text{Li}_2\text{BaP}_2\text{O}_7$  upon UV excitation. Red line (602 nm) dominates the spectrum upon 372 nm excitation. However, the green line dominates the spectrum upon 230 nm excitation. The results are quite interesting from luminescence point of view. Therefore, we suggest a new red, green and blue emitting  $\text{Li}_2\text{BaP}_2\text{O}_7:\text{Tb}^{3+}$  phosphor for pc-LEDs to generate white light.

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## 1. Introduction

Interest has been growing for the last few decades in the development of (In, Ga)N-based light-emitting diode (LED) technology, mainly aimed at advancing solid-state white lighting sources. There are several methods to obtain the white light from LEDs. To acquire white light from LEDs, the methodology requires coupling together several LED chips of discrete colors, using quantum dots (QD) to down-convert higher energy light or making use of phosphors to down-convert near-UV and blue light. The strategy entailing phosphors is considered more promising due to long lifetimes, colour stability, high efficiency, mercury-free, physical lustiness and environmental friendly. Therefore, white light-emitting diodes (w-LEDs) are now looked on as the fourth generation of solid-state lighting devices. Presently, the most accepted approach to acquire white light LED is to assemble a blue diode together with yellow YAG:Ce phosphor but due to problem of thermal quenching and poor colour rendition, an alternative approach, combining a UV chip with red, green and blue phosphors has been suggested and found to be fruitful to overcome the above two problems [1–4]. As host materials, phosphates have proven their place in phosphor industry by virtue of their wide band gap, excellent thermal and chemical stability [5–11]. Another good quality of phosphates is that they can be easily prepared at moderate temperatures though in rare cases very high temperatures are required [5–11]. Recently, several new phosphates like  $\text{LiSrPO}_4:\text{Eu}^{2+}:\text{Tb}^{3+}$  [12],  $\text{KYP}_2\text{O}_7:\text{RE}^{3+}$  (RE = Sm, Tb, Dy) [13],  $\text{KBaPO}_4:\text{Ln}$  (Ln = Eu, Tb, Sm) [14],  $\text{Ca}_{19}\text{Zn}_2(\text{PO}_4)_{14}:\text{Eu}^{3+}$  [15],  $\text{KMLn}(\text{PO}_4)_2:\text{RE}$  (M = Cs, Sr; Ln = Y, La, Lu;  $\text{RE}^{3+}$  = Ce, Eu, Tb) [16] and  $\text{MMgP}_2\text{O}_7:\text{Eu}^{3+}$  (M = Ca, Ba, Sr) [17] have been reported. The spectroscopic properties of these phosphors are quite promising. The spectral features also indicate that these phosphors could be effectively excited in the NUV-region to generate white light. Given these interesting spectral properties of rare earth activated phosphates, we were encouraged to study another rare earth doped phosphate for the purpose of luminescence. There are just six reports about luminescence property of  $\text{Li}_2\text{BaP}_2\text{O}_7$  phosphor [18–23]. In this work we observe that  $\text{Li}_2\text{BaP}_2\text{O}_7:\text{Tb}^{3+}$  phosphor shows intense red emission

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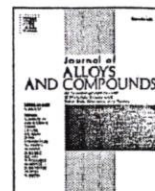
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Contents lists available at ScienceDirect

## Journal of Alloys and Compounds

journal homepage: <http://www.elsevier.com/locate/jalcom>

# Photoluminescence, thermoluminescence and evaluation of some parameters of $\text{Dy}^{3+}$ activated $\text{Sr}_5(\text{PO}_4)_3\text{F}$ phosphor synthesized by sol-gel method



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## ABSTRACT

In this study, we have synthesized  $\text{Dy}^{3+}$  activated  $\text{Sr}_5(\text{PO}_4)_3\text{F}$  (S-FAP) phosphors by sol-gel synthesis method. The synthesized phosphors were characterized by X-ray diffraction pattern (XRD), scanning electron microscopic (SEM), photoluminescence (PL) and thermoluminescence (TL) for structural, morphological and luminescent properties.  $\text{Dy}^{3+}$  activated  $\text{Sr}_5(\text{PO}_4)_3\text{F}$  phosphor shows its characteristic PL emission at 481 nm and 574 nm due to  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$  and  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$  transitions, respectively. TL characteristics of  $\text{Dy}^{3+}$  doped  $\text{Sr}_5(\text{PO}_4)_3\text{F}$  phosphors were taken after irradiation by  $^{60}\text{Co}$  gamma exposure. Two separate TL peaks at 126 °C and 279 °C were observed in case of  $\text{Dy}^{3+}$  doped phosphor.  $\text{Sr}_5(\text{PO}_4)_3\text{F}:\text{Dy}^{3+}$  phosphor was irradiated within a wide range of exposure of 50 Gy to 7 kGy doses. Linearity was found up to 2 kGy and thereafter TL response saturates. Fading study was also carried out over the duration of six weeks for  $\text{Sr}_5(\text{PO}_4)_3\text{F}$  phosphor. Trapping parameters were calculated using Chen's peak shape method, initial rise method and various heating rate method. Glow curve is deconvoluted using computerized glow curve deconvolution program. TL sensitivity of  $\text{Sr}_5(\text{PO}_4)_3\text{F}:\text{Dy}^{3+}$  phosphor is found to be less by a factor of 2.08 than commercially used  $\text{CaSO}_4:\text{Dy}$  phosphor. In order to identify the defect centers formed upon  $\gamma$ -ray irradiation in  $\text{Sr}_5(\text{PO}_4)_3\text{F}:\text{Dy}^{3+}$  phosphor, EPR measurements were carried out on un-irradiated and irradiated phosphors.

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## 1. Introduction

Luminescence is the phenomenon of emission of cold light at normal room temperature. It is well known that there are several types of luminescence, each named for the source of energy that causes it. Thermoluminescence (TL) is one of them, which is mainly found to be occurring in insulator type of substances. As it appeared from its name thermoluminescence that the main source of energy in this process is heat, to trigger luminescence phenomena. As we know that TL is not related to black body radiation since here heat is

used as a stimulating agent for those electrons and holes (trapped between forbidden energy gap) which recombine with each other after getting energy through heat. Thus to occur TL process it is necessary to introduce electron and hole pairs at defect centers through irradiation (ionizing or nonionizing radiation) of the material [1]. Therefore, TL phenomenon of any substance is dependent on the amount of radiation absorbed (also called as dose). This technique is widely used nowadays to measure absorbed amount of dose in radiation protection areas as a TL dosimetry (TLD) [2–4]. It is to be noted that many investigators have investigated a number of TLD materials which are commercially available  $\text{CaSO}_4:\text{Dy}$ ,  $\text{LiF}:\text{Cu,Mg,P}$ ,  $\text{CaF}_2$ ,  $\alpha\text{-Al}_2\text{O}_3$  etc in personal, clinical and environmental dosimetry [5–8]. These mentioned TLD materials are widely used due to their higher sensitivity, thermal stability, less fading and reusability; however, a very less number of TLD materials are available nowadays for use in different field of radiation affected

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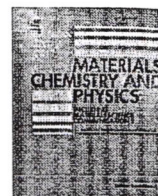
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Efficient resonance energy transfer study from  $\text{Ce}^{3+}$  to  $\text{Tb}^{3+}$  in  $\text{BaMgF}_4$ 

Bhushan P. Kore <sup>a, b, \*</sup>, Sumedha Tamboli <sup>b</sup>, N.S. Dhoble <sup>c</sup>, A.K. Sinha <sup>d</sup>, M.N. Singh <sup>d</sup>,  
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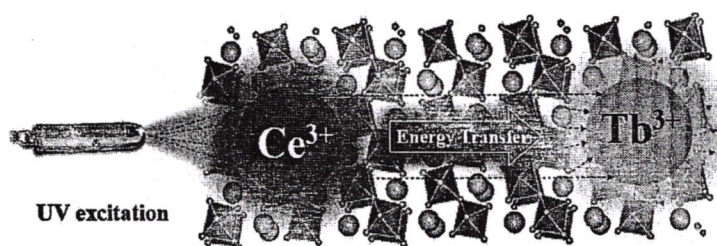
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## HIGHLIGHTS

- $\text{BaMgF}_4:\text{Ce}$ ,  $\text{Tb}$  phosphors was prepared by simple precipitation method.
- The  $\text{Ce}$  co-doped  $\text{BaMgF}_4:\text{Tb}^{3+}$  phosphor show strong PL emission in the green region.
- The efficient green emission is due to the resonance energy transfer from  $\text{Ce}^{3+}$  to  $\text{Tb}^{3+}$ .
- The  $\text{BaMgF}_4:\text{Ce}$ ,  $\text{Tb}$  host has good thermal stability along with good quantum efficiency.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A low temperature precipitation method was employed for the synthesis of green emitting orthorhombic  $\text{BaMgF}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$  phosphors. We investigated the structural, photoluminescence (PL) and energy transfer properties of the  $\text{BaMgF}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$  phosphor. The PL emission spectrum of  $\text{BaMgF}_4:\text{Ce}^{3+}$  shows two unresolved peaks at 315 nm and 336 nm, assigned to the lowest 5d level to the two J-multiplets of the  $4f^1$  configuration of  $\text{Ce}^{3+}$ . Characteristic emission of  $\text{Tb}^{3+}$  was observed at 546 nm which comes in the green region of the visible spectrum. The  $\text{Ce}$  co-doped  $\text{BaMgF}_4:\text{Tb}^{3+}$  phosphor show strong PL emission in the green region, which is due to the resonance energy transfer from  $\text{Ce}^{3+}$  to  $\text{Tb}^{3+}$ . Further, we have calculated the energy transfer parameters and discussed the energy transfer mechanism in detail. The thermal stability and quantum yield of the prepared phosphor was also studied. The obtained results reveal that  $\text{BaMgF}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$  phosphor can be considered as a potential green emitting phosphor for optoelectronic applications.

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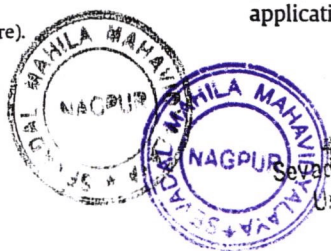
## 1. Introduction

Rare earth (RE) ions doped phosphors have been extensively studied for several decades mainly due to their potential

applications in lighting [1–3]. In most of the RE ions the luminescence originates from 4f states and that can cover entire visible spectrum. The bright emission from RE ions is useful in various applications such as fluorescent lamps, plasma display panels, LEDs, bulk lasers, solar concentrators [4,5] etc. Looking at the importance of energy saving phosphors, rare earth doped/co-doped phosphors are the extensive topic of research owing to their future application in field emission displays (FEDs), fluorescent lamps

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# Preparation and tunable luminescence of microcrystalline $\text{SrMg}_2\text{Al}_{16}\text{O}_{27}:\text{Tb}^{3+}$ and $\text{Eu}^{3+}$ phosphor for solid state lighting

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**Abstract** To understand the mechanism of excitation and the corresponding emission of prepared phosphor for solid state lighting here we discuss here the luminescence properties of  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  doped  $\text{SrMg}_2\text{Al}_{16}\text{O}_{27}$  phosphor for solid state lighting. In this work  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  ion is used as a dopant, and in case of  $\text{Tb}^{3+}$  the excitation and emission spectra indicate that this phosphor can be effectively excited by 353 nm, to exhibit bright green emission centered at 545 nm corresponding to the  $f \rightarrow f$  transition of  $\text{Tb}^{3+}$  ions while in case of  $\text{Eu}^{3+}$  phosphor can be efficiently excited by 396 and observed the emission at 597 nm and 614 nm in addition with analysis of chromaticity coordinates. All the characteristics indicated that  $\text{SrMg}_2\text{Al}_{16}\text{O}_{27}:\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  is a good candidate for solid state lighting industry applications.

## 1 Introduction

Owing to their exceptional optical properties, such as higher luminous effectiveness, energy consumption properties, extended life time and mercury free excitation, white light-emitting diodes are considered to be next generation of solid-state lighting sources. There are various approaches are being available to produce white light with the help of blue/Near ultra-violet light emitting diodes (NUVLEDs) [1, 2]. In 1997, Nakamura reported the production of white LEDs by the arrangement of basic primary color (i.e. green, blue and a red) LEDs [3]. Now a day's interest in research and investigation of suitable phosphor for the generation of LED's based solid-state lighting is extremely increases. It offer the advantages of superior intensity, energy saving and extended life time compare to fluorescent lamps and conventional light bulbs [4, 5]. Because of a great variety of compounds and due to improve the white emission quality in W-LEDs along with expansion of their alignment of UV LEDs with RGB phosphors analyzed [6]. The  $\text{Tb}^{3+}$  luminescence in a new aluminates host material  $\text{MgSrAl}_{12}\text{O}_{17}$  was reported by Panse et al. [7] and has prospective outstanding applications for white LED phosphors near-UV chip. Terbium and europium ions can be stabilized with host material in the trivalent oxidation state. The inclusion and stabilized condition of Tb ions in the prepared material was confirmed by investigation of luminescence mechanism. In our work,  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  doped  $\text{SrMg}_2\text{Al}_{16}\text{O}_{27}$  phosphor was prepared by using combustion synthesis methods and then the prepared phosphor material was further characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL) techniques. Therefore,  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  doped  $\text{SrMg}_2\text{Al}_{16}\text{O}_{27}$  phosphor is the outstanding microcrystalline phosphors for solid state lighting.

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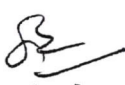
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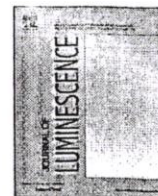
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# A comparative investigation of $\text{Ce}^{3+}/\text{Dy}^{3+}$ and $\text{Eu}^{2+}$ doped $\text{LiAlO}_2$ phosphors for high dose radiation dosimetry: Explanation of defect recombination mechanism using PL, TL and EPR study



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## ABSTRACT

This study describes a comparative analysis of  $\gamma$ -ray irradiated thermoluminescence properties of  $\text{Ce}^{3+}/\text{Dy}^{3+}$  and  $\text{Eu}^{2+}$  doped  $\text{LiAlO}_2$  phosphor.  $\text{LiAlO}_2: \text{Ce}^{3+}/\text{Dy}^{3+}/\text{Eu}^{2+}$  phosphors were synthesized by solution combustion method. The as synthesized phosphors were characterized by X-ray diffraction (XRD) and Scanning electron microscopy (SEM) for structural and morphological study. Rietveld Refinement of XRD patterns were executed by using Fullprof suit software program. Thermoluminescence characteristics of these phosphors show a linear dose response for a wide range of gamma radiation, especially  $\text{Eu}^{2+}$  doped  $\text{LiAlO}_2$  phosphor. The presence of large number of lithium vacancies in  $\text{LiAlO}_2$  phosphor was supposed to be responsible for TL characteristics. Electron paramagnetic resonance (EPR) study of un-doped and  $\text{Ce}^{3+}/\text{Dy}^{3+}/\text{Eu}^{2+}$  doped  $\text{LiAlO}_2$  phosphor was carried out to confirm the presence of  $\text{Eu}^{2+}$  ion and cation, anion vacancies in the host lattice. The responsible defect recombination mechanism for observed TL peak in  $\text{LiAlO}_2$  was developed on the basis of TL and EPR study of irradiated and un-irradiated samples. TL kinetics was studied through glow curve deconvolution, Chen's peak shape method and initial rise method. A good match of kinetic parameters was observed between Chen's peak shape method and IR method. The present phosphors may find application in the dosimetry of high dose ionizing radiation.

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## 1. Introduction

The knowledge of radiation effect on physical, chemical and biological properties of living and non-living things lead to the development of radiation technologies [1,2]. These radiation technologies can be divided in two groups i) dealing with low doses of radiation, such as radiotherapy and ii) dealing with high doses of radiation such as radiation processing. The high dose radiation technologies include material modification, sterilization of medical products, and preservation of agriculture product [1]. All these above mentioned technologies use gamma emitters like  $^{60}\text{Co}$ ,  $^{137}\text{Cs}$  or high energy charge accelerator like electron accelerator providing radiation exposure doses in the range of several kilo grays [1–3]. Ionizing radiations need proper measurement of dose for the better effectiveness of radiation processing. The quality of radiation work also depends on the correct measurement of the absorbed dose in the dose interval

suggested by radiation experts. Thus, need of radiation dosimetry plays a vital role in radiation processing when conducted according to the necessity, directions and the process optimization [4]. The need of high dose measurement is also required at nuclear power stations and in the plant of liquid sludge hygienization [2]. The enormous use of radiation in different areas motivates researchers to develop a suitable dosimetry system according to the area of interest. A number of luminescence based detectors (TLDs) have already been developed for the quality control in radiation process and a large number of novel dosimetric materials are still being investigated [5–7].

The development of lithium aluminate ( $\text{LiAlO}_2$ ) as a radiation detection material has been increased since last one decade [8–10]. The optically stimulated luminescence (OSL) and thermoluminescence (TL) properties of this material make it significant in radiation dose measurements [8–12]. The enriched content of  $^6\text{Li}$  isotopes having a larger capture cross-section for thermal neutron makes it useful in neutron detection as a neutron scintillator [12]. The  $\text{LiAlO}_2$  material is also used as a tritium breeding material in fusion reactor and lattice matching substrate for growing nonpolar GaN or ZnO layers [13,14]. The compound  $\text{LiAlO}_2$  is found to be

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RESEARCH ARTICLE

# Photoluminescence and thermoluminescence of $K_2Mg(SO_4)_2:Eu$ and evaluation of its kinetic parameters

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## Abstract

The  $K_2Mg(SO_4)_2:Eu$  phosphor, synthesized by a solid-state diffusion method, was studied for its photoluminescence (PL) and thermoluminescence (TL) characteristics. The X-ray diffraction (XRD) pattern of the material was matched with the standard JCPDF No. 36-1499. For PL characteristics,  $K_2Mg(SO_4)_2:Eu^{2+}$  showed an emission peak at 474 nm when excited at 340 nm, while it showed  $Eu^{3+}$  emission at 580 nm, and 594 nm splitting at 613 nm and 618 nm for an excitation of 396 nm wavelength due to radiative transitions from  $^5D_0$  to  $^7F_j$  ( $j = 0, 1, 2, 3$ ). The Commission International de l'Eclairage (CIE) chromaticity coordinates were also calculated for the  $K_2Mg(SO_4)_2:Eu$  phosphor, and were close to the NTSC standard values. For the TL study, the prepared sample was irradiated using a  $^{60}Co$  source of  $\gamma$ -irradiation at the dose rate of 0.322 kGy/h for 2 min. The formation of traps in  $K_2Mg(SO_4)_2:Eu$  and the effects of  $\gamma$ -radiation dose on the glow curve are discussed. Well defined broad glow peaks were obtained at 186°C. With increasing  $\gamma$ -ray dose, the sample showed linearity in intensity. The presence of a single glow peak indicated that there was only one set of traps being activated within the particular temperature range. The presented phosphors were also studied for their fading, reusability and trapping parameters. There was just 2% fading during a period of 30 days, indicating no serious fading problem. Kinetic parameters were calculated using the initial rise method and Chen's half-width method. Activation energy and frequency factor were found to be 0.77 eV and  $1.41 \times 10^6 \text{ sec}^{-1}$ .

## KEYWORDS

kinetic parameters, luminescence, phosphor, sulphate, XRD

## 1 | INTRODUCTION

Europium ion, as one of the promising species that provide optical emission in the blue ( $Eu^{2+}$ ) and red colour ( $Eu^{3+}$ ) regions, has been doped into various compounds. The trivalent Eu ion has provided optical devices in red colour regions and many investigations have been conducted using various compounds.<sup>[1]</sup>  $Eu^{3+}$  emission is very useful for studying the nature of metal coordination in various systems due to its non-degenerate emitting  $^5D_0$  state.

To understand the characteristics of thermoluminescence (TL) materials, it is necessary to analyse their glow curves and evaluate their kinetic parameters. Glow curve analysis is useful for dosimetric studies, such as studying TL dose-response for each glow peak and determining the lifetime of trapped electrons in the phosphor.<sup>[2]</sup> The positions,

shapes and intensities of the glow peaks are related to various parameters of the trapping states responsible for TL. The trapping-emitting centres responsible for TL emission were described quantitatively by various kinetic parameters such as activation energy, frequency factor and order of kinetics. Various experimental techniques such as curve fitting methods, Chen's half-width methods, the whole glow peak method, heating rate methods, isothermal decay analysis methods, etc., have been developed to determine these parameters from TL glow curves.<sup>[3,4]</sup> The present paper discusses photoluminescence (PL), and TL characterization and the study of kinetic parameters by two different methods of Eu-doped  $K_2Mg(SO_4)_2$ . The initial rise method of analysis was first suggested by Garlick and Gibson.<sup>[5]</sup> In applying the initial rise method, a graph of  $\ln(I)$  versus  $1/kT$  was made, and a straight line was obtained. From the slope  $-E$  of the line, the activation energy  $E$  was evaluated without any knowledge of the frequency factor  $s$ . Another method often used is Chen's half-width method, also known as the shape of the glow curve method.

Abbreviations: CIE, Commission International de l'Eclairage; LED, light-emitting diode; TLD, thermoluminescent dosimeter; XRD, X-ray diffraction.



RESEARCH ARTICLE

# Dy<sup>3+</sup>-, Sm<sup>3+</sup>-, Ce<sup>3+</sup>- and Tb<sup>3+</sup>-activated optical properties of microcrystalline BaMgP<sub>2</sub>O<sub>7</sub> phosphors

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## Abstract

Photoluminescence (PL) and thermoluminescence (TL) properties of rare earth (RE) ion (RE = Dy<sup>3+</sup>, Sm<sup>3+</sup>, Ce<sup>3+</sup>, Tb<sup>3+</sup>) activated microcrystalline BaMgP<sub>2</sub>O<sub>7</sub> phosphors are presented in this work. Non-doped and doped samples of BaMgP<sub>2</sub>O<sub>7</sub> were prepared using a solid state diffusion method and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), PL and TL. The XRD measurement confirmed the phase purity of the BaMgP<sub>2</sub>O<sub>7</sub> host matrix. The average particle size was found through SEM measurement to be around 2 μm. All activators using the PL technique displayed characteristic excitation and emission spectra that corresponded to their typical f → f and f → d transitions respectively. Thermoluminescence measurements showed that BaMgP<sub>2</sub>O<sub>7</sub>:RE (RE = Dy<sup>3+</sup>, Sm<sup>3+</sup>, Tb<sup>3+</sup>, Ce<sup>3+</sup>) and co-doped BaMgP<sub>2</sub>O<sub>7</sub>:Ce<sup>3+</sup>, Tb<sup>3+</sup> phosphors have also TL behaviour.

## KEYWORDS

BaMgP<sub>2</sub>O<sub>7</sub>, optical properties, phosphor, rare earth ions

## 1 | INTRODUCTION

In recent years, phosphate compounds have come on the scene as an important family of luminescent materials because of their low preparation temperature, high brightness, wide band gap, strong absorption in the UV region, high ultra-violet transmission, stable physical and chemical properties and ease of control over particle size.<sup>[1–8]</sup> It is known that alkali and alkaline earth pyrophosphates have the properties required to act as inorganic phosphor materials.<sup>[9]</sup> Initially, the phosphors of the pyrophosphates family were limited in their use to cathode ray excitation.<sup>[9]</sup> But at the present time UV/X-ray excited pyrophosphate phosphors have also been reported in the literature.<sup>[10–13]</sup> In addition to phosphors as inorganic materials, pyrophosphates are used as fertilizers, catalysts, electrode materials for batteries, and in metal finishing processes, chemical analysis, in preparation of piezoelectrics, ceramics, etc. Pyrophosphates are also important in the chemistry of living cells.<sup>[14]</sup>

Phosphors based on other host families (such as sulphates, nitrides, aluminates, and borates etc.) have also been reported and have interesting characteristics, however there are a few drawbacks related to phosphors based on these host families. For example, sulfide phosphors are thermally unstable and sensitive to moisture.<sup>[6]</sup> The preparation of nitride phosphors often demands sophisticated atmospheric conditions, such as high temperature and high pressure.<sup>[6]</sup>

Moreover, aluminates and borate phosphors generally show lower quantum efficiency.<sup>[6]</sup> Phosphors based on the phosphate family, however, can be prepared at moderate temperatures. They have better thermal and chemical stability when compared with aluminates and borate phosphors.<sup>[15–20]</sup> They have also better quantum efficiency than the latter.<sup>[15–20]</sup> Recently, detailed studies on the thermal stability and quantum efficiency of some well known phosphate phosphors have been reported.<sup>[15–20]</sup> Paulo *et al.* studied the effect of different annealing temperatures on the quantum efficiency of REPO<sub>4</sub>:Eu<sup>3+</sup> (RE = Y, La, Gd) phosphors.<sup>[18]</sup> Lin *et al.* investigated the effect of temperature (i.e., from 25 °C to 300 °C) on luminescence emission of KBaPO<sub>4</sub>:Ln (Ln = Eu, Tb, Sm) and YAG:Ce<sup>3+</sup> phosphors and observed that KBaPO<sub>4</sub>:Ln phosphors are better than the YAG:Ce<sup>3+</sup> above 200 °C.<sup>[17]</sup> The present article reports the optical properties of microcrystalline BaMgP<sub>2</sub>O<sub>7</sub>:Ln<sup>3+</sup> (Ln = Dy, Sm, Ce, Tb) pyrophosphate phosphors. To the best of our knowledge there have been only three reports published on the luminescence properties of BaMgP<sub>2</sub>O<sub>7</sub> i.e., doped with Eu<sup>2+</sup>, Eu<sup>3+</sup> or Mn<sup>2+</sup>.<sup>[21–23]</sup> In these three reports, luminescence due to only Eu<sup>2+</sup>, Eu<sup>3+</sup> or Mn<sup>2+</sup> activators has been discussed. However, we know that Dy<sup>3+</sup>, Sm<sup>3+</sup>, Ce<sup>3+</sup> and Tb<sup>3+</sup> are potential activators in luminescence spectroscopy and to our knowledge there has been not a single report in the literature that describes doping and luminescence of these activators in BaMgP<sub>2</sub>O<sub>7</sub>. This situation motivated us to study Dy<sup>3+</sup>, Sm<sup>3+</sup>, Ce<sup>3+</sup> and Tb<sup>3+</sup> activated luminescence



# Comparison of thermoluminescence characteristics in $\gamma$ -ray and $C^{5+}$ ion beam-irradiated $LiCaAlF_6:Ce$ phosphor

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**ABSTRACT:** We compare the thermoluminescence (TL) behavior of  $Ce^{3+}$  ion-activated  $LiCaAlF_6$  exposed to  $\gamma$ -rays and a carbon ion beam. The reported phosphor is synthesized using an in-house precipitation method with varying concentrations of activator ion and is characterized by X-ray diffraction (XRD) and TL. Rietveld refinement is performed to study the structural statistics. The TL glow curve consists of a prominent glow peak at 232°C with three shoulders at 115, 159 and 333°C when exposed to  $\gamma$ -rays from a  $^{60}Co$  source. When exposed to a  $C^{5+}$  ion beam, the TL glow curve consists of five peaks with peak temperatures near 156, 221, 250, 287 and 330°C, and is found to vary slightly with changing fluence. Glow curve convolution deconvolution (GCCD) functions are applied to the TL curves for complete analysis of the glow curve structure and TL traps. The order of kinetics ( $b$ ), activation energy ( $E$ ) and frequency factor are determined using Chen's peak shape method and theoretical curves are drawn using GCCD functions. A track interaction model (TIM) is used to explain the sublinearity/saturation at higher fluences. Ion beam parameters are analyzed using Monte-Carlo simulation-based SRIM-2013 code. Copyright © 2016 John Wiley & Sons, Ltd.

**Keywords:** thermoluminescence; carbon ion beam; Monte-Carlo simulation-based SRIM-2013; TIM model

## Introduction

Ionizing radiation has been used in tumor treatment for a number of decades and photon radiotherapy (RT) is extensively used for the treatment of cancer (1). Recently, along with photon RT, heavy ion RT has attracted a lot of interest in the field of cancer treatment. Heavy ions show low angular, energy straggling and improved dose conformations compared with photons. Thus, heavy ion RT is more effective than photon RT because of its sharp increase in dose within a well-defined depth and the rapid fall in dose beyond the maximum penetration depth of heavy ion (2). An additional feature of heavy ions is the strong increase in their linear energy transfer (LET) in the affected region (3–5).

Among the heavy ions, carbon ions are most useful due to their biological and physical properties. In addition, the significantly increased LET in the affected region makes carbon ions a great tool for use with all types of tumors, especially those surrounded by critical structures. Carbon ion RT works in similar way to traditional photon RT, in which a tumor is targeted with the goal of destroying the cancerous cells. The size of carbon ions allows them to cause more disruption and create irreparable damage when they hit a cancer cell. Unlike traditional RT, carbon ion treatments cause relatively little damage to healthy cells in the path to the tumor. Scientists can control the penetration depth and tailor the 'shape' of the energy deposited by the carbon ions to closely match the shape of a tumor. Once the ions reach the tumor, energy is delivered within a very narrow zone, almost like an explosion in the tumor. This treatment provides doctors with important options when targeting tumors near sensitive structures such as the brain.

Carbon ion therapy leads to damage that is much more complex and difficult for the cancer cell to repair (3,6–8). Hence, great precision and accuracy in ion beam dosimetry are needed when treating humans. This requires the development of ion beam dosimeters that satisfy characteristic dosimetric properties (9). Thus, there is

increasing demand for the dosimetry of charged particle beams because they are increasingly used for diagnostic and therapeutic purposes (4,5,10). Commonly used dosimeters such as  $LiF:Cu,Mg,P$  and  $CaSO_4:Dy$  are not standardized for use in ion dosimetry and there is the opportunity to develop new materials tailored for ion dosimetry.

The effect of a carbon ion beam on micro- and nanocrystalline  $CaSO_4:Dy^{3+}$  has been reported previously by Salah (11). Nanoparticles of  $CaSO_4:Dy$  are found to have less sensitivity than their micro-particle counterparts, but are more efficient at higher doses because microparticles saturate at a lower dose. Recently, Kore et al. (12) reported  $CaMg_3(SO_4)_4:Dy^{3+}$  phosphor for carbon ion dosimetry, which shows 3.5 times more sensitivity than commercial  $CaSO_4:Dy$  Thermoluminescent dosimeter (TLD) phosphor. Other researchers have also reported the use of phosphor in carbon ion dosimetry (13,14).

$Ce^{3+}$ -activated  $LiCaAlF_6$  is a well-known phosphor with diverse applications in solid-state tunable lasers and scintillators (15–19). A lot of work has been done on colquirite-type  $LiCaAlF_6$  phosphors explaining their Photoluminescence (PL), Thermoluminescence (TL) and Optically Stimulated Luminescence (OSL) properties triggered by different activator ions (20–24). However, no studies on ion-beam irradiated  $LiCaAlF_6:Ce$  have been found. In this study, we report the effect of a  $C^{5+}$  ion beam on the TL properties of  $Ce$ -activated  $LiCaAlF_6$ .

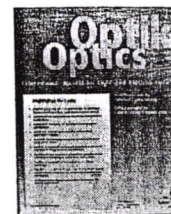
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# Photoluminescence investigation of trivalent rare earth activated $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$ phosphors for solid state lighting

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## ABSTRACT

In this paper we report the photoluminescence (PL) characteristics of  $\text{Dy}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  doped  $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$  phosphors prepared by wet chemical method. Prepared phosphors were characterized by X-ray powder diffraction (XRD), scanning electron microscope (SEM), color co-ordinates and photoluminescence (PL) properties. The emission spectra of  $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}:\text{Dy}^{3+}$  phosphor show the characteristic emission of  $\text{Dy}^{3+}$  ions peaking at 478 nm and 573 nm ( $\lambda_{\text{ex}} = 390$  nm), owing to transitions of  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$  and  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$  receptively. Under 396 nm excitation the  $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}:\text{Eu}^{3+}$  phosphor shows emission at 594 nm and 616 nm due to  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transitions of  $\text{Eu}^{3+}$  ions respectively. When  $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}:\text{Tb}^{3+}$  phosphor was excited by 380 nm, the emission spectrum showed intense green band at 545 nm due to  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition in  $\text{Tb}^{3+}$  ion. The PL emission spectrum of  $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}:\text{Sm}^{3+}$  phosphors by 405 nm excitation gave an emission at 562 nm ( $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ ), 598 nm ( $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ ) and 643 nm ( $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ ). The CIE color coordinates indicated that all the above phosphors were suitable as a white light-emitting phosphor. SEM studies of the phosphors show that grain size of the powders prepared by the wet chemical method is about ten micrometers range. From the obtained results it can be concluded that  $\text{Dy}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  doped  $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$  phosphors are potential candidates for solid state lighting applications in green technology.

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## 1. Introduction

Rare-earth activated inorganic luminescence materials having special attention for developing new devices such as X-ray imaging, radiation dosimetry, solid state lasers, fiber amplifiers and biosensors [1,2]. It is well known that Nakamura et al. in 1997 developed the W-LEDs by combining blue LED chips and yellow-emitting phosphor [3]. The commercial YAG:Ce yellow phosphors became available by Nichia Chemical Co. in 1997. This phosphor when excited by blue light gives emission in yellow region [4,5]. YAG:Ce has a low color-rendering index due to lack of red component. Therefore it is necessary to develop new red phosphors having excitation in the near-UV region or blue region [6,7]. The above disadvantage could be overcome by developing a new stable phosphor by using a mixture of red and yellow emission with strong excitation band at around 400 nm, having high color rendering index. The LED light source is the best potential light sources when compared

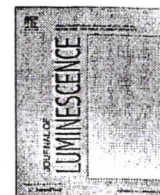
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## Full Length Article

Effect of  $\text{Ce}^{3+}$  ion on  $\text{Dy}^{3+}$  or  $\text{Mn}^{2+}$  in  $\text{KMgSO}_4\text{Cl}$  synthesized by centrifuge methodNita Shinde<sup>a</sup>, N.S. Dhoble<sup>b</sup>, S.C. Gedam<sup>c,\*</sup>, S.J. Dhoble<sup>a</sup><sup>a</sup> Department of Physics R.T.M. Nagpur University, Nagpur 440033, India<sup>b</sup> Department of Chemistry, Sevadal Mahila Mahavidyalaya, Nagpur 440018, India<sup>c</sup> K.Z.S. Science College, Kalmeshwar, Nagpur 441501, India

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## ABSTRACT

In this paper effect of  $\text{Ce}^{3+}$  ion on  $\text{Dy}^{3+}$  and  $\text{Mn}^{2+}$  ions in microcrystalline  $\text{KMgSO}_4\text{Cl}$  host prepared by ethanol (centrifuge technique) method has been discussed. In  $\text{KMgSO}_4\text{Cl}$  sample X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL) characteristics have been studied. Powder X-ray diffraction analysis shows the crystalline nature of the phosphor prepared by this new route. The morphological structures of the samples were conducted using SEM technique. An average crystallite size was found to be 5  $\mu\text{m}$ . Photoluminescence in  $\text{KMgSO}_4\text{Cl}:\text{Ce}^{3+}$  is observed at 324 nm and 344 nm along with red emission broad band at around 644 nm. In  $\text{KMgSO}_4\text{Cl}:\text{Ce}, \text{Dy}$  phosphor  $\text{Ce}^{3+}$  emission around 324 and 344 nm overlaps rather well with  $\text{Dy}^{3+}$  excitation. The addition of  $\text{Ce}^{3+}$  showed higher photoluminescence (PL) intensity for the  $\text{Dy}^{3+}$  emissions around 482 and 576 nm excited via  $\text{Ce}^{3+}$  ions at 284 nm due to  $^4\text{F}_{9/2}$  to  $^6\text{H}_{15/2}$  and  $^6\text{H}_{13/2}$  levels.  $\text{Ce}^{3+} \rightarrow \text{Mn}^{2+}$  energy transfer process occurs in  $\text{KMgSO}_4\text{Cl}$  host.  $\text{KMgSO}_4\text{Cl}:\text{Mn}$  does not give PL at 284 nm excitation but for co-doped samples with cerium,  $\text{Mn}^{2+}$  ions exhibits efficient fluorescence at around 560 nm due to  $^4\text{T}_1-^6\text{A}_1$  transition.  $\text{KMgSO}_4\text{Cl}:\text{Dy}$  or  $\text{KMgSO}_4\text{Cl}:\text{Mn}$  directly exciting does not show any emission while addition of  $\text{Mn}^{2+}$ , enhances red emission of  $\text{Ce}^{3+}$  at 644 nm. The CIE co-ordinates of  $\text{KMgSO}_4\text{Cl}:\text{Ce}$ ;  $\text{KMgSO}_4\text{Cl}:\text{Ce}, \text{Dy}$  and  $\text{KMgSO}_4\text{Cl}:\text{Ce}, \text{Mn}$  phosphors reveals that the emission colour varies from blue to deep-red. Hence this material may be a potential lamp phosphor.

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## 1. Introduction

By continuing the study on the same  $\text{KMgSO}_4\text{Cl}$  host by adopting new ethanol synthesis method (centrifuge technique), we could successfully prepare it. Previously we have worked on  $\text{KMgSO}_4\text{Cl}:\text{Ce}$ ;  $\text{KMgSO}_4\text{Cl}:\text{Ce}, \text{Dy}$  and  $\text{KMgSO}_4\text{Cl}:\text{Ce}, \text{Mn}$  (S.C. Gedam, S. J. Dhoble, S. V. Moharil J. Lumin. 124 (2007) 120–126) by using wet chemical method. The luminescence properties of co-activator compounds have received considerable interest. The main interest has been received concerned with the utilization of efficient energy migration on sensitizer to activator. Energy transfer phenomena have led to the development of new and efficient photoluminescence materials. Cerium doped materials usually show strong broad-band PL. The luminescence is very strongly dependent on the host lattice and can occur from the ultraviolet to the red region of the electromagnetic spectrum.  $\text{Ce}^{3+}$  emission results from 5d to 4f type of transition. As far as the

spectroscopy is concerned, the  $\text{Ce}^{3+}$  ground state [1,2] is split between  $^2\text{F}_{5/2}$  and  $^2\text{F}_{7/2}$  and these are the only levels possible for 4f configuration. f–f transition in  $\text{Ce}^{3+}$  is in the IR region. At room temperature, they occur as unresolved bands with a maximum at about 2200–2300  $\text{cm}^{-1}$  and half width of 250–300  $\text{cm}^{-1}$ . The excited state, above  $^2\text{F}_{7/2}$  level, belongs to 5d configuration in the form of broad bands. Energy transfer process from Ce to activators in different host matrices is well known. Broad band emitters are often used to sensitize the luminescence of RE ions. Optical transitions within a 4f<sup>n</sup> configuration are so strongly forbidden that they appear in the absorption spectra as very weak. However, excitation resulting in high light output can be achieved by exciting a different ion (i.e., sensitizer) with an optically allowed transition which transfers the excitation energy to the RE activator.

Efficient energy transfer from the broad (i.e.  $\text{Ce}^{3+}$ ) to the narrow-line emitter (i.e.,  $\text{Dy}^{3+}$  or  $\text{Mn}^{2+}$ ) is possible only between nearest neighbours in the crystal lattice and optimal spectral overlap. If the spectral overlap is small, only partial energy transfer is possible.  $\text{CaF}_2:\text{Mn}$  does not give any fluorescence under the UV excitation while  $\text{CaF}_2:\text{Ce}$  gives a characteristic  $\text{Ce}^{3+}$  fluorescence emission with UV

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# Thermoluminescence and EPR study of $K_2CaMg(SO_4)_3:Dy$ phosphor: the dosimetric application point of view

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## Abstract

A detailed investigation of the thermoluminescence (TL) properties of  $\gamma$ -ray and  $C^{5+}$  ion beam irradiated  $K_2CaMg(SO_4)_3:Dy$  (KCM) phosphor was carried out. KCM was irradiated by 50 and 75 MeV energy  $C^{5+}$  ion beams with a fluence range of  $15 \times 10^{10}$  ions  $cm^{-2}$  to  $30 \times 10^{12}$  ions  $cm^{-2}$ . The TL glow curves along with the response curves of these phosphor samples were analyzed and compared with commercial  $CaSO_4:Dy$  phosphor. The TL glow curves of the phosphor exposed to  $\gamma$ -rays from  $^{60}Co$  and  $^{137}Cs$  sources were also examined in this study for comparative analysis. Theoretical analysis of the glow curves of the  $C^{5+}$  ion beam and  $\gamma$ -ray irradiated samples was performed using the glow curve deconvolution method. SRIM/ TRIM simulations were performed in order to identify the ion beam profile, range, distribution, etc. The enhancement in the intensity of the low temperature glow peak is explained with the help of an energy level model and the decrease in TL intensity with increasing ion fluence is also explored in detail. The radicals produced after irradiation were verified using the electron paramagnetic resonance (EPR) technique. The effects of temperature and microwave power on the EPR signal are also studied.

**Keywords:** swift heavy ions, dosimetry, thermoluminescence, radiations, glow curves

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(Some figures may appear in colour only in the online journal)

## 1. Introduction

Thermoluminescence (TL) is one of the most commonly used techniques in the dosimetry of ionizing radiation [1–4]. It is also one of the simplest methods for dose determination, in which the dose absorbed by the sample is estimated using the TL output during TL measurements. The light output depends

upon the dose absorbed by the material, an increase in the dose will lead to an increase in the TL emission, within certain limits of doses. The TL technique is also used in dosimetry of heavy ion beams [5, 6]. Phosphors show different TL responses to conventional photon beams and heavy charge particle beams [7–9]. This variation in TL response is due to the differences in dose distribution of the radiation used







# Novel photoluminescence properties of $\text{Eu}^{3+}$ doped chlorapatite phosphor synthesized via sol-gel method



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## ABSTRACT

Chlorapatite phosphors having formula  $\text{Ca}_{(9.97-x)}(\text{PO}_4)_6\text{Cl}_{1.94-x}\text{Eu}^{3+}$  ( $x = 0.05 \text{ mol\%}$ ,  $0.1 \text{ mol\%}$ ,  $0.3 \text{ mol\%}$ ,  $0.5 \text{ mol\%}$ ,  $0.7 \text{ mol\%}$  and  $1 \text{ mol\%}$ ) were synthesized by sol-gel synthesis method. X-ray diffraction (XRD) pattern of the synthesized sample was obtained to ensure the formation of compound. Crystallographic study was done by performing Rietveld refinement analysis. Surface morphology of the compound was examined by obtaining scanning electron microscopy (SEM) images. Photoluminescence (PL) emission spectra show intense emission peak at 574 nm and relatively less intense peaks at 601 nm, 623 nm and 629 nm with 461 nm excitation. Emission peak located at 574 nm is very intense in this compound which is rarely observed for  $\text{Eu}^{3+}$  ions doping. PL decay is obtained and site selective transition of  $\text{Eu}^{3+}$  ion in apatite host is discussed. Commission International de l'Eclairage (CIE) chromaticity color coordinates of this phosphor were calculated. CIE-chromaticity color coordinates shows yellowish-orange emission of the phosphor.

## 1. Introduction

Europium ion is vigorously studied activator in the field of luminescence and extremely useful as a dopant in phosphors for LED and display devices, sensor [1–4]. It can exist in  $\text{Eu}^{3+}$  as well as  $\text{Eu}^{2+}$  forms.  $\text{Eu}^{3+}$  ion possess interconfigurational 4f-4f transitions which are forbidden transitions and  $\text{Eu}^{2+}$  ion possess 4f-5d transition which is allowed transition. 4f-4f transitions of  $\text{Eu}^{3+}$  ions are hypersensitive transition [5–7]. Depending on the chemical environment present around the crystallographic site, which is available for doping of  $\text{Eu}^{3+}$  ions, some forbidden transitions become allowed and blue-green-red emissions can be seen. Site dependent emissions of  $\text{Eu}^{3+}$  ions is utilized by researchers to study local structural symmetry in host [8,9]. In  $\text{Eu}^{3+}$  doped compound, absorption of energy can be done either by 4f-4f transition or charge transfer (CT) transition. Excitation peak corresponding to CT transition is called as CT band. CT band is the result of interaction of  $\text{O}^{2-}$  ions with  $\text{Eu}^{3+}$  ions. The position of the CT band varies depending on the band gap of host materials [10]. Thus, by selecting the appropriate host material, desired absorption and emission spectrum of  $\text{Eu}^{3+}$  ions can be obtained and structural study can be done.

In present work, photoluminescence of  $\text{Eu}^{3+}$  ions in chlorapatite system has been studied. Apatite family of compounds is an important class of inorganic compounds and contains large number of compounds

with different elemental constituents. Apatites are widely distributed minerals in igneous rock. They have the general formula,  $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$ , where X is F (fluorapatite, FAp), OH (hydroxyapatite, OHAp), or Cl (chlorapatite, ClAp). Ca can be replaced by Sr, Ba, Na and Pb. OHAp is the mineral of bone and teeth [11]. Apatite lattice is very tolerant for substitution of rare earth elements or transition metal ions. Therefore, doping of activator ions can be done very easily without disturbing the overall stability and crystal structure of the host.  $\text{Ca}_5(\text{PO}_4)_3\text{F}:\text{Mn}^{2+}$ ,  $\text{Sb}^{3+}$  (Ca-FAp) compound is the well-known lamp phosphor used in fluorescent lamp industry [12]. Therefore, rare earth doped apatite is always an interesting topic for researchers which motivates us to carry out this work.

The calcium chlorapatite  $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$  (ClAp) is an important compound of apatite family.  $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$  exists as two polymorphs: a monoclinic phase with space group P21/b at low temperature and the typical hexagonal phase with space group P6<sub>3</sub>/m after thermal treatment above 350 °C. In calcium chlorapatite, there are two crystallographically distinct Ca atoms having C<sub>2</sub> and C<sub>3</sub> symmetry [13]. Rare earth doped calcium chlorapatite compound is synthesized by some researchers and different strategies were developed for the synthesis of chlorapatite because synthesis techniques can change the photoluminescence property of compound [14]. Zhang et al. synthesized  $\text{Eu}^{2+}$  and  $\text{Tb}^{3+}$  co-doped  $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$  phosphor by conventional solid state synthesis method [15]. Kim et al. studied photoluminescence

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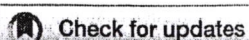
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# On the study of the $C^{6+}$ ion beam and $\gamma$ -ray induced effect on structural and luminescence properties of Eu doped $LiNaSO_4$ : explanation of TSL mechanism using PL, TL and EPR study

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The present paper reports on the  $\gamma$ -ray and  $C^{6+}$  ion beam induced effect on the structural and luminescence properties of Eu doped  $LiNaSO_4$  phosphors synthesized via wet the chemical method. The material was irradiated by  $^{60}Co$  and  $^{137}Cs$   $\gamma$ -rays and 75 MeV  $C^{6+}$  ions in a fluence range varying from  $2 \times 10^{10}$  to  $1 \times 10^{12}$  ion per  $cm^2$ . The ion induced modified properties were investigated using X-ray diffraction (XRD), micro-Raman spectroscopy, photoluminescence (PL), thermoluminescence (TL) and electron paramagnetic resonance (EPR) studies. The XRD and micro-Raman results confirm the loss of crystallinity and elongation of the lattice parameters after ion beam irradiation. The presence of both divalent as well as trivalent states of Eu ions at multiple sites of  $LiNaSO_4$  is observed by PL study. Irradiation of the  $LiNaSO_4:Eu$  phosphor with a  $C^{6+}$  ion beam modifies the population of the valence state of the doped rare earth Eu ion and enhances the TL sensitivity of this phosphor. The nature of the prominent TL glow curve is identical for both  $\gamma$ -ray and  $C^{6+}$  ion beam irradiated materials while additional deep trap levels appear in the latter due to the formation of several types of cation and anion vacancy. The electron paramagnetic resonance (EPR) technique also supports the presence of the Eu ion at multiple sites and provides information regarding several types of radical produced after  $\gamma$ -ray and  $C^{6+}$  ion irradiation. Finally, a mechanism is presented for the thermally stimulated luminescence phenomenon on the basis of our observed results from the PL, TL and EPR studies. The reason behind ion beam irradiation induced modification of the TL properties and enhancement of luminescence intensity is also explained in this report.

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## 1. Introduction

Irradiation of rare earth-doped phosphors with photons or heavy charged particles (HCPs) induces some modification in the structural and optical properties of the phosphors. Such irradiation induced modifications have been widely studied in the past few decades for their everyday applications in the fields of nuclear science, materials science and natural science.<sup>1–3</sup> HCPs are regarded as the best tool to explore the mechanism of ion interaction with matter and the consequent formation of new trap centers or point defects in the materials.<sup>4</sup> Heavy ion beam irradiations lead to changes in the optical, structural,

mechanical, electrical, and chemical properties of materials in a precise way due to the deposition of highly energetic charged particles with wide ranges of energy.<sup>1–5</sup> When energetic ion beams interact with materials they lose their energies in two modes, (i) nuclear and (ii) electronic stopping. Nuclear stopping is dominant at low energies while electronic stopping is dominant at high energies where the displacement of atoms due to elastic collisions is insignificant.<sup>6</sup> Electronic energy loss causes intense electronic excitation or ionization of atoms by inelastic collisions along the ion trajectory. This process creates new defect centers in the materials. HCP irradiation may also result in the loss of crystallinity due to the creation of lattice defects in the host matrix of studied materials.<sup>7</sup> The defects produced in the target materials can also be influenced by the types of ion used as well as the ion energy and fluences. There are several studies on the formation of point defects, new trap centers, and the rearrangement of existing defect centers after swift heavy ion beam (SHI) irradiation which gives a clear indication about the improved luminescence properties of

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# Impact of $C^{5+}$ ion beam on Dy activated $Sr_2B_5O_9Cl$ TL phosphor

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## Abstract

$Sr_2B_5O_9Cl$ : Dy phosphor was synthesized by modified solid state diffusion method and the impact of  $C^{5+}$  ion-beam on its TL behavior was studied in detail. Phosphor was annealed at 1000 °C for obtaining single phase host. XRD technique was used to confirm the formation of the material and was matched with JCPDS-27-08835. The synthesized phosphor was characterized for photoluminescent spectra. Characteristic emission at 484 nm ( $^4F_{9/2} \rightarrow ^6H_{15/2}$ ) and 575 nm ( $^4F_{9/2} \rightarrow ^6H_{13/2}$ ) confirms the presence of  $Dy^{3+}$  ions in the  $Sr_2B_5O_9Cl$  host matrix. Further TL properties of the synthesized material were studied for fluence range  $1.5 \times 10^{11}$ – $30 \times 10^{11}$  ion/cm<sup>2</sup> (i.e. 40.14–802.9 kGy dose) of  $C^{5+}$  ion-beam (75 MeV) and were found to show the non linear behavior between a dose range 40.14–802.9 kGy. TL glow curve for  $Sr_2B_5O_9Cl$ :Dy irradiated with  $C^{5+}$  ion-beam (75 MeV) was compared with that of  $\gamma$ -ray irradiated phosphor. TRIM/SRIM calculations were performed to correlate the changes in TL properties of  $Sr_2B_5O_9Cl$ :Dy phosphor.

## 1 Introduction

The measurement of radiation doses is one of the important areas of research due to the fact that radiation above a permissible dose is harmful to human kind. Thermoluminescence is a very useful technique to estimate the quantity of absorbed dose of ionizing radiations. Practically, thermoluminescence dosimeter (TLD) badges are used for environment, personal, space, health and many more radiation monitoring applications [1–4]. Today, there are a number of commercial TL dosimeters available for users as TLD badges and are mostly based on oxides, fluorides and sulphates. However, each of these dosimeters has their own strengths and shortcomings in certain areas such as in the low or high radiation zones. For this reason continuous efforts have been made by the research community worldwide to develop new materials and to improve dosimetric

properties of already available materials as efficient TLD material in the form of low  $Z_{eff}$  (tissue equivalence) as well as high  $Z_{eff}$  that can be used in different areas with low or high levels of radiations. Most of the phosphors can be used as TLDs within a specific range of radiation doses and not for all doses from very low to very high range because it depends on various factors including linearity, precision, dose rate, fading, reproducibility, and others. Thus there is a need to explore more sensitive materials that show linearity of TL response in the large range, materials which are energy independent, thermally stable and have low fading. Moreover there is a continuous demand for efficient TL dosimeters for monitoring high dose levels of swift heavy ions (SHI) that are growing daily as these ions are used extensively in medical applications.

Ion beam therapy is found to have an important role in the treatment of cancer as compare to the conventional photon beam. In conventional beam irradiation the dose deposition decreases in proportion to the penetration depth whereas in ion beams it gradually increases, and then decreases rapidly beyond a sharply defined maximum known as the Bragg peak near the end of the range of the ion beams. Bragg peak therapy offers the promise of excellent dose localization for treatment of tumors. Therefore, ion beams are important for treating tumors located deeply inside the body and is a better option for cancer therapy to avoid the high risk surgery and the side effects of medicinal drugs. Among various types of ion beams, carbon ion beams particularly are

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# Luminescence properties of nanocrystalline $\text{Mg}_2\text{P}_2\text{O}_7\text{:Eu}$ phosphor

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## Abstract

Thermoluminescence (TL) measurements were carried out on europium (Eu) doped magnesium pyrophosphate ( $\text{Mg}_2\text{P}_2\text{O}_7$ ) nanopowders using gamma irradiation in the dose range of 0.1 to 3 kGy. The powder samples were successfully synthesized by chemical co-precipitation synthesis route. The formation and crystallinity of the compound was confirmed by powder X-ray diffraction (PXRD) pattern. The estimated particle size was found to be in nanometer scale by using Debye Scherer's formula. A scanning electron microscopy (SEM) study was carried out for the morphological characteristics of as synthesized  $\text{Mg}_2\text{P}_2\text{O}_7\text{:Eu}$  phosphor. Photoluminescence (PL) study was carried out to confirm the presence of the rare-earth ion and its valence state. The TL analysis of synthesized samples were performed after the irradiation of  $\text{Mg}_2\text{P}_2\text{O}_7\text{:Eu}$  with cobalt-60 ( $^{60}\text{Co}$ ) gamma rays. The high and low intensity peaks of TL glow curve appeared at around 400 K, 450 K, 500 K and 596 K respectively. The appreciable shift in peak positions has been observed for different concentrations of Eu ion. The trapping parameters, namely activation energy ( $E$ ), order of kinetics ( $b$ ) and frequency factor ( $s$ ) have been determined using thermal cleaning process, peak shape (Chen's) method and glow curve deconvolution (GCD) functions.

## KEYWORDS

high dose,  $\text{Mg}_2\text{P}_2\text{O}_7$ , nanomaterial, thermoluminescence

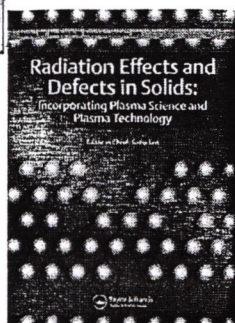
## 1 | INTRODUCTION

Thermoluminescence (TL) has gained lots of popularity since the sixteenth century due to its applications in various fields such as radiation therapy, dosimetry, geology, space research and other research related areas.<sup>[1]</sup> TL is the thermally stimulated emission of light from an insulator or a semiconductor following the previous absorption of energy from ionizing or non-ionizing radiation.<sup>[2]</sup> The thermoluminescent properties of a number of materials has been investigated so far and it is observed that mixed alkali/alkaline phosphate set up a class of TL phosphors with worthy performances, particularly when doped with appropriate activators or impurities.<sup>[3]</sup> Several materials

like  $\alpha\text{-Al}_2\text{O}_3\text{:C}$ ,  $\text{LiF:Ti,Mg}$ , and  $\text{CaSO}_4\text{:Dy}$  due to their exceptional thermoluminescent properties such as high TL efficiency, thermal stability, high sensitivity and reproducibility, are now widely used as thermoluminescent dosimeters (TLDs) in different fields of applications.<sup>[4]</sup> Numerous applications of radiation in wide areas have motivated towards the development of radiation dosimetric materials according to the area of interest. Several luminescence based detectors (TLDs) were developed for the detection of radiation as well as quality control in radiation processing, and many novel dosimetric materials are still being researched.<sup>[5,6]</sup> However, the saturation of TL response at high dose (above 1 kGy) of irradiation is a major concern for TL detectors like  $\text{LiF:Mg,Cu,P}$ ,  $\text{MgB}_4\text{O}_7\text{:Dy}$  and  $\text{CaSO}_4\text{:Dy}$ .<sup>[4,7]</sup> The main reason of TL saturation at high-dose exposure is due to the limited capacity of electron traps which gets filled with free electrons created after ionization of phosphor materials.<sup>[8]</sup> Moreover, this problem can be resolved by using a radiation resistant material or materials having a

Abbreviations used: CTB, charge transfer band; EDX, energy dispersive X-ray; Eu, europium; GCD, glow curve deconvolution;  $\text{Mg}_2\text{P}_2\text{O}_7$ , magnesium pyrophosphate; PL, photoluminescence; SEM, scanning electron microscopy; TL, thermoluminescence; XRD, X-ray diffraction.





## Radiation Effects and Defects in Solids Incorporating Plasma Science and Plasma Technology

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### Effect of $\gamma$ -radiation on TL, ESR and evaluation of trapping parameters of $K_2Ca(SO_4)_2:X$ ( $X = Dy$ or $Eu$ ) phosphors

Archana Deshpande, S. C. Gedam, N. S. Dhoble, S. J. Dhoble, V. G. Rane & R. M. Kadam

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# Luminescence study of LiMgBO<sub>3</sub>:Dy for γ-ray and carbon ion beam exposure

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## Funding Information

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## Abstract

LiMgBO<sub>3</sub>:Dy<sup>3+</sup>, a low  $Z_{\text{eff}}$  material was prepared using the solution combustion method and its luminescence properties were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), thermoluminescence (TL), photoluminescence (PL), Fourier transform infrared spectroscopy, and electron paramagnetic resonance (EPR) techniques. Reitveld refinement was also performed for the structural studies. The PL emission spectra for LiMgBO<sub>3</sub>:Dy<sup>3+</sup> consisted of two peaks at 478 due to the  $^4F_{9/2} \rightarrow ^6H_{15/2}$  magnetic dipole transition and at 572 nm due to the hypersensitive  $^4F_{9/2} \rightarrow ^6H_{13/2}$  electric dipole transition of Dy<sup>3+</sup>, respectively. A TL study was carried out for both the γ-ray-irradiated sample and the C<sup>5+</sup> irradiated samples and was found to show high sensitivity for both. Moreover the γ-ray-irradiated LiMgBO<sub>3</sub>:Dy<sup>3+</sup> sample showed linearity in the dose range 10 Gy to 1 kGy and C<sup>5+</sup>-irradiated samples show linearity in the fluence range  $2 \times 10^{10}$  to  $1 \times 10^{11}$  ions/cm<sup>2</sup>. In the present study, the initial rise method, various heating rate method, the whole glow curve method, glow curve convolution deconvolution function, and Chen's peak shape method were used to calculate kinetic parameters to understand the TL glow curve mechanism in detail. Finally, an EPR study was performed to examine the radicals responsible for the TL process.

## KEYWORDS

ESR, LiMgBO<sub>3</sub>, tissue equivalent material, trapping parameters

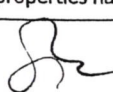
## 1 | INTRODUCTION

Boron-based materials show interesting thermoluminescence (TL) properties when exposed to ionizing radiation<sup>[1,2]</sup>. The luminescence properties of lithium borate and magnesium borate in both microcrystalline and nanocrystalline forms have been studied previously<sup>[1–4]</sup>. Recently, researchers who studied lithium magnesium borate phosphor found that it was useful for applications in dosimetry<sup>[5,6]</sup>.

To date, only a few studies on LiMgBO<sub>3</sub> have been reported<sup>[5]</sup>. Recently, the TL properties of rare earth ion (RE = Tb, Gd, Dy, Pr, Mn, Ce, Eu)-doped lithium magnesium borate (LMB) prepared by the

the solid state diffusion method, have been documented<sup>[6]</sup>. LMB:Tb<sup>3+</sup> showed the best results with a stable TL peak at 240°C. LMB:Tb<sup>3+</sup> was about four times more sensitive than TLD-100. Optical properties of LMB glasses, doped with Dy<sup>3+</sup>, Sm<sup>3+</sup> ions have been studied<sup>[7]</sup>. Photoluminescence properties of LMB:Eu and LMB:Eu,Bi have also been studied in detail<sup>[8]</sup>. LiMgBO<sub>3</sub>:Dy<sup>3+</sup> in its polycrystalline form has been prepared using a novel solution combustion method and its TL sensitivity was found to be half compared with commercial TLD-100 and showed a high degree of fading of 30% after 20 days<sup>[9]</sup>. Furthermore, LiMgBO<sub>3</sub>:Dy<sup>3+</sup> in its nanocrystalline form has been prepared using the combustion method and its structural and optical properties have been studied<sup>[10]</sup>.



  
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## REVIEW

WILEY LUMINESCENCE  
The Journal of Biological and Chemical Luminescence

# Versatility of thermoluminescence materials and radiation dosimetry – A review

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## Abstract

Thermoluminescence (TL) materials exhibit a wide range of applications in different areas such as personal dosimetry, environmental dosimetry, medical research etc. Doping of different rare earth impurities in different hosts is responsible for changing the properties of materials useful for various applications in different fields. These materials can be irradiated by different types of beams such as  $\gamma$ -rays, X-rays, electrons, neutrons etc. Various radiation regimes, as well as their dose-response range, play an important role in thermoluminescence dosimetry. Several TL materials, such as glass, microcrystalline, nanostructured inorganic materials and recently developed materials, are reviewed and described in this article.

## KEYWORDS

dosimetry, glass, ionizing radiation, phosphors, thermoluminescence

## 1 | INTRODUCTION

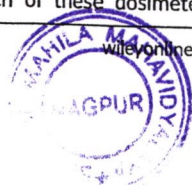
Radiation comes from natural, as well as anthropogenic sources. The human response to radiation from different sources is subject to great scientific uncertainty and intense controversy. Radiation can be used in the treatment of diseases such as cancer, in which even small doses of radiation might do some harm. Many factors are involved in finding the effects of radiation exposure to health, such as the amount of energy deposited in the tissue and the ability of the radiation to generate harm. The regulated international value for the equivalent dose for a member of the general public is 1 mSv/year.<sup>[1,2]</sup> Therefore, there is a need to measure even small doses in the environment and very high doses at times of accident such as radiation leakage in isotopic laboratories and moreover for the treatment of cancer.

Thermoluminescence dosimetry (TLD) is one of the most important techniques used to quantify the absorbed dose, in addition to other techniques based on solid-state dosimetry such as radiation-induced absorbance (RIA).<sup>[3,4]</sup> In practice, TLD badges are used for different radiation monitoring applications.<sup>[5,6]</sup> Therefore, there are many oxide, fluoride and sulphate-based phosphors in the form of TL badges available commercially. However, each of these dosimeters is not

suitable for all low or high radiation zones. Therefore, continuous efforts is being made by researchers worldwide to develop new materials and to improve the dosimetric properties of existing materials to be used as efficient TLD materials over a wide range of radiation doses.<sup>[7–10]</sup>

## 2 | DEVELOPMENTS IN TLD MATERIALS

Thermoluminescence (TL) was first described by Farrington Daniels and colleagues<sup>[11]</sup> when introducing LiF as a TL material and that was later patented as TLD-100 by the Harshaw Chemical Company.<sup>[12,13]</sup> Many new dosimetric phosphors have been reported over the last few decades that have different efficiencies for different dose ranges of radiation. Nanophosphors have a potential role in many R&D areas such as medical,<sup>[14,15]</sup> accidental,<sup>[16]</sup> retrospective,<sup>[17,18]</sup> personal,<sup>[19]</sup> thermal neutron<sup>[20]</sup> dosimetry, solid-state lighting<sup>[21,22]</sup> and 2D optical stimulated luminescence (OSL) mapping.<sup>[23]</sup> Many standard commercial dosimeters are now available, the most famous being LiF: Mg,Cu,P (TLD-700H), Al<sub>2</sub>O<sub>3</sub> (TLD- 500), CaSO<sub>4</sub>:Dy (TLD-900) and CaF<sub>2</sub>:Dy (TLD-200).<sup>[24–26]</sup> Each of these phosphors cannot be used





# Intense green-, red-emitting $\text{Tb}^{3+}$ , $\text{Tb}^{3+}/\text{Bi}^{3+}$ -doped and $\text{Sm}^{3+}$ , $\text{Sm}^{3+}/\text{La}^{3+}$ -doped $\text{Ca}_2\text{Al}_2\text{SiO}_7$ phosphors

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## Abstract

This paper focuses on an optical study of a  $\text{Tb}^{3+}/\text{Bi}^{3+}$ -doped and  $\text{Sm}^{3+}/\text{La}^{3+}$ -doped  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  phosphor synthesized using combustion methods. Here,  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Sm}^{3+}$  showed a red emission band under visible light excitation but, when it co-doped with  $\text{La}^{3+}$  ions, the emission intensity was further enhanced.  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Tb}^{3+}$  shows the characteristic green emission band under near-ultraviolet light excitation wavelengths, co-doping with  $\text{Bi}^{3+}$  ions produced enhanced photoluminescence intensity with better colour tunable properties. The phosphor exhibited better phase purity and crystallinity, confirmed by X-ray diffraction. Binding energies of  $\text{Ca}(2p)$ ,  $\text{Al}(2p)$ ,  $\text{Si}(2p)$ ,  $\text{O}(1s)$  were studied using X-ray photoelectron spectroscopy. The reported phosphor may be a promising visible light excited red phosphor for light-emitting diodes and energy conversion devices.

## KEYWORDS

$\text{Ln}^{3+}$  ions, combustion synthesis, X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy photoluminescence

## 1 | INTRODUCTION

Due to the vast increase in demand for energy from industry and for households and commercial purposes, the level of power generated based on coal and fossil fuel technologies is growing rapidly and hence the levels of  $\text{CO}_2$  and other harmful gases in our environment are increasing. This increase has a detrimental effect on human health and the health of other living animals due to changes in water, soil and air qualities. Many research groups and organizations are making increased efforts to develop both environmentally friendly energy generation and energy-saving technologies for the sustainable development of mankind. Many existing technologies developed by scientists have been proposed and proven in practice to have the capacity to produce new and renewable sources of energy generation that are based on geothermal energy, wind energy, solar energy, and hydrothermal energy etc.<sup>[1]</sup> These natural resources are available depending on the geographical and geological resources of each country. Of the different natural resources, the Sun is the main contributor to life on Earth and development of the global environment. Natural sunlight is available everywhere and in larger amounts in most countries when

compared with other resources. Therefore solar photovoltaic technology is the best alternative for energy generation, as it uses a green and non-polluting source.<sup>[2]</sup> We should not only think about environmentally friendly sources of energy, but also focus on energy-saving technologies. In the area of power generation and utilization, some energy is used for indoor or outdoor lighting, and for decoration etc. Therefore there is a second challenge to develop low-cost, non-toxic, energy-saving products that are environmentally sustainable. Compared with lighting devices used over the past few decades such as incandescent or compact fluorescent lamps (CFL), light-emitting diodes (LED) are an emerging lighting source for the 21st century based on their special merits of long operating lifetime, energy-saving potential, high brightness, and much reduced toxicity compared with incandescent or fluorescent light sources.<sup>[3]</sup> Therefore, indirectly, they help to control the level of greenhouse gases in the atmosphere due to their energy-saving capabilities. LEDs have many advantages and are a much safer alternative to current lighting devices used at commercial and industrial levels.<sup>[4-6]</sup> White LEDs (wLED) are made using two methods: (1) by combining near-ultraviolet (NUV) LED chips with RGB phosphors; and (2) by combining blue and yellow phosphors and





## RESEARCH ARTICLE

WILEY LUMINESCENCE  
The Journal of Biological and Chemical Luminescence

# Study of thermoluminescence in turtle shell fossils using radiation dosimetry

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### Abstract

The present study describes for the first time thermoluminescence (TL) characterization of turtle shell. A fossil shell was collected from the Dongargaon area in the Chandrapur district of Maharashtra, India. TL was recorded and a comparative study of TL for the above material was performed to understand the special TL characteristics of the shell. The shell was irradiated with <sup>60</sup>Co γ-radiation to study its TL properties. The sample displayed two good TL peaks at 135°C and 255°C. A linear dose-response curve for the irradiated sample was produced for the dose range 0.79–28.5 kGy; this sample of turtle shell (fossil) may be useful as a high dose dosimetry phosphor in this range. This geological sample was further characterized using X-ray diffraction to confirm its phase structure and by scanning electron microscopy, Fourier transform infrared and wavelength dispersive X-ray fluorescence spectroscopy to determine morphology, vibration, and elemental composition as ppm or percentage of the sample, respectively. Kinetic parameters of the TL glow peak were calculated using three different methods.

### KEYWORDS

gamma rays, high dose dosimetry, thermoluminescence, XRD

## 1 | INTRODUCTION

Luminescence is the emission of cold light at normal room temperature. There are many types of luminescence such as photoluminescence<sup>[1]</sup>, mechanoluminescence<sup>[2]</sup>, electroluminescence<sup>[3]</sup>, magneto-luminescence<sup>[4]</sup>, cathodoluminescence<sup>[5]</sup>, bioluminescence<sup>[6]</sup>, and thermoluminescence<sup>[7]</sup>. Each emission is named after its source of energy. TL is one type of luminescence that is mainly emitted from insulators. The main source of energy in this process is heat, which activates the luminescence.<sup>[8]</sup> TL is totally dependent on the amount of radiation absorbed by the dose substance. This method is widely used to measure the dose absorbed in a radiation protection area as in TL dosimetry.<sup>[9–11]</sup> LiF:Mg,Ti<sup>[12]</sup>, CaSO<sub>4</sub>:Dy<sup>3+</sup><sup>[13]</sup> and CaSO<sub>4</sub>:Tm<sup>[14]</sup> etc. are commercial TL materials used as medical, personal, or environmental dosimeters. Many commercial thermoluminescent dosimeter (TLD) materials are used extensively due to their high sensitivity, thermal stability, limited fading, and

reproducibility, however few TLD materials are used in the specialized field of radiation affected regions.<sup>[15–19]</sup> Therefore increased interest has been generated in find natural geological natural materials that could replace commercial phosphors (Figs 1–18).

Thermoluminescence is a useful phenomenon to characterize traps and lattice defects in broad band gap materials in which light is radiated from heated materials due to the release of trapped stored electrons.<sup>[20]</sup> The released electrons recombine at luminescence centres, giving out a glow. From this TL glow peak, information on trapping parameters such as trap depth or activation energy of the charge trap, and the trap attempt-to-escape frequency, known as the frequency factor, can be gained. For use in dosimetry, the TL peak should be generated at a high temperature, around 473 K. Dosimetric properties of TL materials mainly rely on trapping parameters such as activation energy (E), frequency factor (s), order of kinetics (b) and peak temperature (T<sub>p</sub>) of the glow curve.<sup>[21–25]</sup> Many techniques such as Chen's peak shape method, the initial rise method, the whole glow curve



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## Thermoluminescence study in fossils of dinosaur bones and eggshells

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### Abstract:

In this paper thermoluminescence (TL) characterization of fossils of sauropod dinosaur bone, dinosaur eggshells and associated sediments are recorded for the first time. The fossil bone was collected from the Bagwanya intertrappean sediments in Dhar district of Madhya Pradesh. TL was recorded followed by <sup>60</sup>Co gamma rays exposure at different doses. Fossils of dinosaur bone, dinosaur eggshells and associated sediments were irradiated by <sup>60</sup>Co gamma rays with different doses from 0.15 kGy to 19 kGy. The linear dose response curve of irradiated sample was obtained for dose range from 0.15 kGy to 9.5 kGy. These geological samples were further characterized by XRD for the confirmation of phase, scanning electron microscope (SEM), FT-IR and WD-XRF for the determination of elemental composition for ppm to percentage level.

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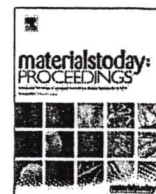
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# Synthesis and characterization of $\text{Eu}^{3+}$ doped $\text{Ca}_9\text{La}(\text{PO}_4)_5(\text{SiO}_4)\text{FCl}$ fluoroapatite phosphor for white LED

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## ABSTRACT

The fluoroapatite  $\text{Ca}_9\text{La}(\text{PO}_4)_5(\text{SiO}_4)\text{FCl}$ :1 mol%  $\text{Eu}^{3+}$  phosphor was synthesized by conventional solid state reaction. In the present work keeping concentration of  $\text{F}_2\text{Cl}_2$  constant and  $(\text{PO}_4)^{3-}$  of the material was replaced by  $(\text{MoO}_4)^{3-}$ . The phase purity and surface morphology was evaluated through X-ray diffraction and scanning electron microscope technique. The emission and excitation spectra were investigated using photoluminescence spectroscopy. The excitation and emission spectra indicate that prepared phosphor effectively excited by 278 nm, exhibits emission peak at 595 nm and 616 nm corresponds to yellow and red colour attributes to  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transitions respectively. The above result reveals prepared phosphor is excellent red phosphor in white light emitting diode application.

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## 1. Introduction

Recently in comparison with conventional incandescent or fluorescent lamp white light emitting diode (w-LED) receive promising attention in the field of solid state technology due its unique characteristics includes, intense luminous efficiency, long operational stability, mercury free, eco-friendly, low power consumption reveals wide application prospects [1–3]. In general, white LEDs (w-LEDs) available in market can be manufactured by combining yellow emitting phosphor with blue InGaN chip. However this type of w-LEDs suffer limitation includes low colour rendering index (CRI) and high correlated color temperature (CCT) due to deficiency of sufficient red emission [4,5]. This limitations is overcome by adopting alternative approach for the formation w-LEDs, by means of coupling of near-ultraviolet (n-UV) InGaN-based chip with tri-color (RGB) phosphor, but still has disadvantage of low efficiency due to re-absorption of blue light by red and green phosphor [6]. It leads to development of alternative red or tunable phosphor with excellent stability and suitable excitation wavelength in the

n-UV region. Recently, apatite-type based phosphor received more attention as a host luminescence materials owing to their remarkable luminescent efficiency and excellent chemical and thermal stability [7,8].

The compounds belongs to apatite family will be iso-structural in nature, compose of hexagonal symmetry (space group of  $\text{P6}_3/\text{m}$ ) consisting general formula  $\text{A}_{10}[\text{PO}_4]_6\text{Z}_2$  where A- indicates divalent cations includes  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  etc. Z- represent F, Cl, Br or O. With consideration of structural morphology  $[\text{PO}_4]^{3-}$  can be substituted by  $[\text{SiO}_4]^{4-}$ ,  $[\text{BO}_4]^{5-}$  and  $[\text{VO}_4]^{3-}$  [6,9,10]. The compounds with apatite structure reveals the capability of substitution by versatile ions and forming the changeable solid state solution apatite structure, attributes to the tunable luminescence followed by excellent luminescent properties, hence gain more interest for the synthesis novel inorganic framework with new compound belong to apatite structure.

In the present work we report the synthesis of  $\text{Ca}_9\text{La}(\text{PO}_4)_5-x(\text{MoO}_4)_x(\text{SiO}_4)\text{F}_2\text{Cl}_2$ :1mol%  $\text{Eu}^{3+}$  fluoroapatite type phosphor by solid state reaction method, further  $[\text{PO}_4]^{3-}$  of the host is replaced by  $[\text{MoO}_4]^{3-}$  and their luminescent properties are investigated. The formation of as-prepared phosphor was further confirmed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis.

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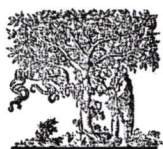


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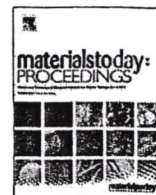




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# Investigating thermoluminescence properties of $\text{Na}_{14}\text{Al}_{12}\text{Si}_{13}\text{O}_{51}:\text{Dy}^{3+}$ phosphor for oxygen ion beam exposure

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## ABSTRACT

The  $\text{Na}_{14}\text{Al}_{12}\text{Si}_{13}\text{O}_{51}:\text{Dy}^{3+}$  phosphor is synthesized by combustion method and prepared sample was characterized by X-ray Diffraction, SEM, FT-IR and Thermoluminescence (TL) techniques. TL characteristics show the quenching at 3 mol% of  $\text{Dy}^{3+}$  ion activated  $\text{Na}_{14}\text{Al}_{12}\text{Si}_{13}\text{O}_{51}:\text{Dy}^{3+}$  phosphor with single TL glow peak 154 °C at higher temperature. Prepared phosphor material was irradiated oxygen ion beam at different fluences range from  $5 \times 10^{10}$  to  $1 \times 10^{14}$  ions/cm<sup>2</sup>. Chens peak method and computerized glow curve deconvolution method was used to evaluate the trapping parameters namely, activation energy, frequency factor, kinetic order associated with the main glow curve in  $\text{Na}_{14}\text{Al}_{12}\text{Si}_{13}\text{O}_{51}:\text{Dy}^{3+}$  phosphor after irradiation.

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## 1. Introduction

Numerous techniques is available to prepare phosphors such as solid state reaction [1], wet chemical methods [2], solution combustion [3], sol-gel [4], spray pyrolysis [5], co-precipitation method [6], heterogeneous precipitation method [7], chemical vapor deposition etc. Among wet chemical methods, 'solution combustion synthesis' has different advantages. It requires simple apparatus and the materials used are more economical [8]. It requires low energy, short time and this technique may also be employed to turn out standardized, high-purity, crystalline oxides. The nature of crystalline, surface area and agglomeration of the synthesized products are primarily governed by flame temperature during combustion which itself depends on the nature of the fuel and the fuel to oxidizer ratio [9]. It is known that, a good fuel should react nonviolently without producing venomous gasses and act as a complexing agent for metal ions. While the solid state reaction method has several shortcomings such as prolonged reaction time, larger size grain growth and poor homogeneity.

The combustion synthesis process is to dissolve metal nitrate and fuel in water, and then to heat the solution in a microwave

oven. The fuel and metal nitrate decomposing and give flammable gases such as  $\text{NH}_3$  and  $\text{NO}_2$ , respectively. After the solution reaches the point of spontaneous combustion, it begins burning and becomes a solid, which burns at high temperature. The combustion is not finished until all the flammable substances are all burned out and it turns out to be a loose substances which show voids, pores, and high friable formed by the escaping gases during the combustion reaction.

Thermoluminescence (TL) has been a dynamic field of research in the present decade because of its broad function potential [10,11]. Its most remarkable application has been in its utilization in radiation dosimetry. Ionizing radiation dosimeters, which depend on the thermoluminescence properties of materials, have helped in the arrangements of numerous dosimetric issues due to their long time stockpiling limits, autonomy of portion with radiation forces, ease with which estimations are done and light weight [12].

Thermoluminescence is the production of light (generally in the visible region) when a TL phosphor already exposed to ionizing radiation ( $\gamma$ ,  $\beta$ , X) is heated. The plot of light production with time at dissimilar temperatures is known the glow curve and the area below the glow curve can be associated to the dose of radiation. The glow curve not only supports accurate estimation of the dose, it can also assist in maintaining the superiority of dose estimation

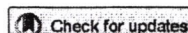
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# Luminescence characteristics of $O^{6+}$ ion beam and $\gamma$ -ray irradiated $Ca_9La(PO_4)_5(SiO_4)F_2:Eu$ phosphor

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## ABSTRACT

Fluorapatite  $Ca_9La(PO_4)_5(SiO_4)F_2:Eu$  with variable molar concentrations of  $Eu^{3+}$  (0.05–1.0 mol%) were synthesised by the solid-state reaction method and their photoluminescence (PL), thermoluminescence (TL) characteristics were studied after irradiating the samples with  $\gamma$ -rays and 75 MeV  $O^{6+}$  ion beam. The formation of the material was confirmed using X-ray diffraction pattern followed by Scanning electron microscopy and Fourier transform infra-red (FTIR) spectrum. The morphology of the synthesised powder was observed to be polycrystalline constituted by microcrystalline particles. FTIR spectrum shows characteristic bands,  $563\text{ cm}^{-1}$  for bending vibration  $\nu_4$  and  $1035\text{ cm}^{-1}$  for stretching vibration  $\nu_3$ . PL spectra show absorption bands at 395 and 466 nm corresponding to  $^7F_0 \rightarrow ^5L_6$  and  $^7F_0 \rightarrow ^5D_2$  transitions and the emission band was seen at around 595 and 616 nm describing  $^5D_0 \rightarrow ^7F_j$  transitions ( $j = 1, 2$ ). Furthermore, TL glow curves of both  $\gamma$ -rays and 75 MeV  $O^{6+}$  ion beam irradiated samples show a prominent peak at around  $145^\circ\text{C}$  with a small hump at around  $245^\circ\text{C}$ . The concentration 0.2 and 1 mol% was found to be the best concentration for studying TL properties of  $Ca_9La(PO_4)_5(SiO_4)F_2:Eu$  irradiated with  $\gamma$ -rays and 75 MeV  $O^{6+}$  ion-beam respectively.

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$Ca_9La(PO_4)_5(SiO_4)F_2$ ; thermoluminescence; photoluminescence; w-LEDs; phosphor

## 1. Introduction

Over the past few years, many inorganic compounds activated by rare earth metals, such as silicates, phosphates, borates, aluminates and sulphides, have attracted great attention for their applications in different fields (1–13). Furthermore, these days, the synthesis of different novel phosphors has become the current topic of the research community due to their excellent luminescent properties required for solid-state lightening. Some of these competent phosphors are Apatite-type phosphors with favourable chemical and thermal stability and excellent luminescent properties (14). Apatite compound represents a similar structure as the natural mineral fluorapatite  $Ca_{10}(PO_4)_6F_2$ . It is having general chemical formula as  $A_{10}(PO_4)_6Z_2$ , where A represents cations such as  $Ca^{2+}$ ,  $Mn^{2+}$ ,  $Ba^{2+}$ ,  $Sr^{2+}$ ,  $Fe^{2+}$ ,  $Mg^{2+}$  and  $Pb^{2+}$  and Z represents F, Cl, Br or O. Moreover,  $[PO_4]^{3-}$  can also be replaced



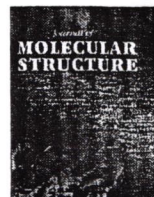
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# Synthesis of novel $\text{Eu}^{2+}$ activated $\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$ down-conversion phosphor for near UV excited white light emitting diode

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CIE chromaticity diagram

## ABSTRACT

In the present paper, we have successfully synthesized  $\text{Eu}^{2+}$  activated  $\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$  phosphor by two-step solid-state reaction method at high temperature (800 °C). Pure crystalline formation, morphological behavior, and their vibration bonds of synthesized  $\text{Eu}^{2+}$  activated  $\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$  phosphor were verified by the X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Fourier transform Infrared Spectrum (FT-IR). The photoluminescence (PL) spectrum and CIE coordinate with color purity also characterized. In PL emission spectra clearly represented that broad excitation band from 250 nm to 400 nm ranged. The center of this PL excitation spectra observe at 326 nm, but some parts of these spectra lies to 350 nm–400 nm. This excitation wavelength is very useful for the generation of white light because it may be used as near UV light. PL emission represents broad emission spectra from 400 nm to 550 nm centred at 440 nm. Most part of these PL emission spectra lies in the blue region of the spectrum. PL spectra arise from the transitions between the 5d and 4f orbital's transition of  $\text{Eu}^{2+}$  ions. EVI parameters such as Stokes Shift ( $\Delta E_s$ ), the Huang-Rhys factor (S), effective phonon energy ( $\hbar\omega$ ) and the Zero-phonon line (ZPL) are calculated. In our present work, we are calculated that the value of Huang–Rhys factor constant (S) is 3.74 that means coupling is intermediately strong. CIE chromaticity coordinate of  $\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}:\text{xmol}\%\text{Eu}^{2+}$  [x = 0.5, 2.0, 3.0, 5.0, 7.0, 10mol%] phosphor were also calculated by using OSRAM SYLVANIA color calculator 1931. By using these CIE chromaticity coordinate was calculated the value of color purity for each concentration of  $\text{Eu}^{2+}$  ions. After seeing all results of synthesized phosphor material we are concluded that it may be a better option used as commercial phosphor for obtaining white light. So it may be a promising candidate for NUV WLEDs.

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## 1. Introduction

In the age of digitization, the energy shortage more times felt when the electrical power is generated on this planet is inefficiently consumed for lighting applications. If energy is not utilized judiciously and wisely for lighting then many problems are clearly viewed on the planet because of the world population daily increased and industrialization regularly improved [1,2]. Rare earth activated inorganic phosphor has attracted a lot of attention due to their excellent features. Rare earth activated inorganic phosphor widely applied in the field of luminescence and their research has a high impact on the energy and environmental sectors [3–5]. It is

also widely used in the field of Hg free fluorescent lamps, plasma display panels, indoor lighting, cathode-ray tubes, solar cell, fingerprint detection, biosensing, phototherapy, plant growth, white light-emitting diodes (WLEDs) and Dosimetric applications [3–10]. Solid-state lighting (SSL) based devices are predicted to play a crucial role in the coming few years. They offer to save huge amounts of electrical energy and reduce carbon emissions by almost 28 million metric tons per year globally [11]. In recent years, phosphor converted white light-emitting diodes has revealed extraordinary features and it becomes the best choice in lighting technology due to their advanced technology and excellent properties such as compact size, high luminous efficiency, energy savings, long operation life-time, and environment-friendliness, etc [2,12–14], which promise significant reductions in power consumption and pollution from fossil fuel power plants [12]. Generally, LEDs are used as an indicator, rear lamps for vehicles,

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*Tailoring the luminescent properties  
of  $\text{Ca}_9\text{La}(\text{PO}_4)_5(\text{SiO}_4)\text{F}_2:1 \text{ mol\%Eu}^{3+}$   
phosphor via doping of chloride, molybdate,  
vanadate, sulfate, and tungstate ions*

**Chaitali M. Mehare, Yatish R. Parauha,  
Vibha Chopra, Sudeshna Ray,  
N. S. Dhoble, Chandan Ghanty &  
S. J. Dhoble**

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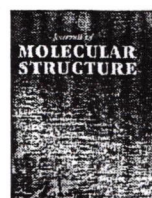


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# Tunable luminescence of $\text{Eu}^{3+}$ , $\text{Sm}^{3+}$ and $\text{Dy}^{3+}$ doped $\text{Na}_2\text{CaMg}(\text{PO}_4)_2$ phosphor for optical applications

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## ABSTRACT

In this work  $\text{Na}_2\text{CaMg}(\text{PO}_4)_2$  and  $\text{Na}_2\text{CaMg}(\text{PO}_4)_{2-x}(\text{SO}_4)_x$  doped with europium, samarium and dysprosium phosphors were synthesized by combustion method using urea as a fuel along with its optical, structural and morphological investigations which may be applicable for solid state lighting and near-UV excited LED. The phase homogeneity of the phosphor was established by X-ray powder diffraction (XRD) and characterized by scanning electron microscopy (SEM), photoluminescent (PL) spectroscopy and room temperature FTIR spectrum. The photoluminescence (PL) properties were investigated under ultraviolet (UV) ray excitation. Preliminary studies showed that the phosphor might be promising candidate as a light-conversion phosphor for the optical system. The luminescence intensity is enhanced considerably by tuning the host matrices after core-shell formation due to degree of decrease of non-radiative rates rising from surface sagging bonds and surpassing agent.

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## 1. Introduction

At present, solid state lightning (SSL) employs light-emitting diodes to produce white light because of their mercury-free, environmental friendliness, low energy consumption, high durability over the conventional incandescent and halogen lamp [1,2]. In 1991 Nakamura [3] provided a first improvement in solid state lightning (SSL) research in the field of white light-emitting diodes by his discovery of blue light-emitting diode (LED). Far along, in 1996, the first white LED was fabricated which used yellow phosphor (YAG:Ce) combined with blue GaN LED [4]. The above reported techniques of generating white light has certain shortcomings such as low color rendering index, radiance effect etc. Consequently, to overcome these shortcomings the alternative techniques to produce white light has been utilized by combining blue, green, red phosphor with UV LED [5].

Phosphates based phosphors have pronounced compensating attention in recent years because of their significant thermal, structural assortment and a moderately short wavelength of optical absorption power. In the midst of them,  $\text{Na}_2\text{CaMg}(\text{PO}_4)_2$  phosphor was first designated by Fuchs et al. [6]. Subsequently Alkemper [7]

described that the structure of  $\text{Na}_2\text{CaMg}(\text{PO}_4)_2$  was interconnected to the cluster of cations and  $[\text{PO}_4]$  tetrahedral in the glaserite structure as well, which has a monoclinic structure and a space group of P21/c. Later, Yonesaki and collaborators described the structure and spectroscopic properties europium doped  $\text{Na}_2\text{MMgP}_2\text{O}_8$  (M: Ba, Sr, Ca) [8]. Lü et al. also reported the spectroscopic properties of europium doped blue-emitting  $\text{Na}_2\text{CaMg}(\text{PO}_4)_2$  phosphors [9]. There is only a solitary report that designates the luminescent properties of  $\text{Ce}^{3+}$  activated  $\text{Na}_2\text{CaMg}(\text{PO}_4)_2$  phosphors [10]. Normally, phosphors are prepared by the outmoded solid state reaction method. This method naturally needs high temperature, time-consuming heating process and consequent crushing for long time. The crushing procedure recompenses the phosphor planes, subsequently results in the loss of emission intensity. Consequently the combustion synthesis has fascinated considerable attention since it is beneficial in attaining the unique chemical configurations with exclusive properties, outstanding purity and moderately low reaction temperature, ensuing in more homogeneous products, and it is also probable to prepare phosphors in the smaller size [11].

To the best of our knowledge, no attention has been paid to the luminescent properties of  $\text{Na}_2\text{CaMg}(\text{PO}_4)_2:\text{Eu}^{3+}, \text{Dy}^{3+}, \text{Sm}^{3+}$  and very few reports are available on these particular phosphors.

In our work,  $\text{Eu}^{3+}, \text{Dy}^{3+}, \text{Sm}^{3+}$  doped  $\text{Na}_2\text{CaMg}(\text{PO}_4)_2$  and

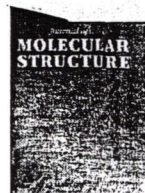
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# Photoluminescence and thermoluminescence characteristics of $\text{CaAl}_2\text{Si}_4\text{O}_{12}:\text{Dy}^{3+}$ new phosphor prepared by combustion synthesis



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## ABSTRACT

The present study reported synthesis of  $\text{Dy}^{3+}$  activated  $\text{CaAl}_2\text{Si}_4\text{O}_{12}$  phosphor via combustion techniques. The formation of crystal structure and surface morphology was analysed by X-ray diffraction pattern and scanning electron microscopy. The photoluminescence spectrum reveals, the prepared phosphor material exhibits an excellent emission at 422 nm, with two peaks around 479 nm (blue region) and 575 nm (yellow region) monitor at excitation wavelength of near UV 369 nm. In addition, CIE color chromaticity confirms the emission locate at the blue light region, revealed suitability of prepared phosphor in UV excitable blue emission for white light emitting diode. The Thermoluminescence characterization of prepared phosphor irradiated with a  $^{60}\text{Co}$   $\gamma$ -ray source at dose rate of 7.2 kGy/hr was further carried out using a Nucleonix TL 1009I TL reader. The tapping parameter such as activation energy (E) and frequency factor (s) was calculated using Ilich's method.

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## 1. Introduction

The crucial need of energy saving and environmental protection issue, facilitate the research on the development of white light-emitting diodes (w-LEDs) for lighting due to their unique characteristics includes, long life-span, high luminous efficiency, good operational stability, energy saving, fast switching, color quality as well as environmental-friendly characteristics which can expected to replace conventional source of light for world-wide in near future [1–5]. Recently, the development of inorganic compounds, especially the rare-earth-doped luminescent materials, has been received more attention owing to their potential applications in the field of lamp industries, field emission display (FEDs), radiation dosimetry, solid state laser and white light-emitting diodes (WLEDs) [6–10]. In the recent year there is extensive investigation of phosphors are already carried out includes aluminates [11], orthosilicates [12], nitrides [13,14], oxides [15,16], sulphides [17] etc. Normally, the initial composition of the host materials, dopant concentrations and processing conditions define the luminescent characterization of rare earth doped activated materials [18]. Among the various reported host phosphors, the alumina-silicate have received more attention owing to its numerous merit such as ex-

cellent luminous efficiency, long life time, low cost and remarkable physical and chemical stability [19,20]. Initially, first w-LED was invented by combination of blue LED with yellow phosphor ( $\text{YAG}:\text{Ce}^{3+}$ ) however poor color rendering index and high correlated color temperature limit its further commercialization [21]. Further approach adopted is to combine UV LED with RGB (red, green, blue) phosphor but it's lower luminescent efficiency owing to strong absorption of blue light by red and green component of phosphors which further hindered its utilization which intensively drive the attention toward the development of single phase white light emitting phosphor [22,23]. A single-host white-emitting phosphor usually reveals broad or multiple emission peaks in the visible region and hence paid crucial inclination for development of novel broadband or multi-peak emitting UV or n-UV excitable w-LED with color stability [24,25]. In recent decades, the rare earth doped activated phosphor gain prime position in various filed such as lighting, photosynthesis enhancement, and photodynamic for cancer therapeutics [26–28]. The trivalent  $\text{Dy}^{3+}$  ions exhibits two intense peaks in blue and yellow region at about wavelength 479 nm corresponding to the  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$  and 575 nm corresponding to the  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$  transition representing its potential application for white light emission [29,30]. The silicate host phosphor doped with  $\text{Dy}^{3+}$  ions shows wide application for generation of white light by simply varying the ratio of blue and yellow part of intensities [31,32]. Moreover it plays as very important role in many long lasting phosphor such as  $\text{BaAl}_2\text{Si}_2\text{O}_8$

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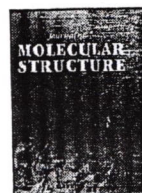
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## Thermoluminescence study of sodium aluminosilicate phosphors

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## ABSTRACT

Sodium aluminosilicates  $\text{NaAlSi}_2\text{O}_6$ : Dy and  $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}$ : Eu has been synthesized using Combustion method. The formation of  $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}$ : Eu phosphor was confirmed by XRD, SEM and FTIR analysis. Thermoluminescence properties of  $\text{NaAlSi}_2\text{O}_6$ : Dy and  $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}$ : Eu after irradiating with 75 MeV  $\text{O}^{6+}$  ion beam have been studied and are found to be similar. Both the phosphors show single TL glow peak that is desirable for good dosimeter. Further both  $\text{NaAlSi}_2\text{O}_6$ : Dy and  $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}$ : Eu shows linear TL response for fluence range  $1 \times 10^{11}$  ions/cm<sup>2</sup> to  $1 \times 10^{12}$  ions/cm<sup>2</sup>. The trapping parameters for both the samples were studied using Chen's peak shape method, Initial rise method and Ilich method and found to have good agreement with each other. So, Sodium aluminosilicates  $\text{NaAlSi}_2\text{O}_6$ : Dy and  $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}$ : Eu can be useful in this particular range for their applications in radiation dosimetry.

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## 1. Introduction

Pyroxene mineral, Jadeite with composition  $\text{NaAlSi}_2\text{O}_6$  is recognized as the gemstone Jade. It is basically an ornamental mineral, known for its green varieties. It is a silicate of sodium and aluminium [1] It has excellent physical properties of higher hardness, good luster etc [2–4]. Jadeite, as microcrystalline powder was synthesized for the first time in 1948 [5], then different techniques such as high pressure method [6–8], ultra high pressure and high temperature polymerization method, ion injection method, high pressure and high temperature (HPHT) method [9–11] were used. The attention was paid to explore HPHT method. Later, Jadeites were prepared under 5 GPa pressure and properties were found to be similar as natural Jadeite [12]. Then pressure of 5 GPa– 5.5 GPa and temperature 1300 °C– 1500 °C [13] and pressure of 3.5 GPa and temperature range 1000 °C– 1400 °C [1] was used to prepare Jadeites to get improved properties. Further, theoretical simulation calculations were carried out successfully [14–19]. Moreover structural properties of Jadeite were studied using plane – wave pseudopotential density functional theory method [8]. Very recently, our group has synthesized  $\text{NaAlSi}_2\text{O}_6$ : Dy using combustion method for the first time and their TL properties were studied using  $\gamma$ -ray exposure [20].

Further, by changing the elemental composition Hexa Aluminosilicate with chemical formula  $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}$  was obtained [21]. It has two different sizes of cavities to be used as nano- molecular sieving material and environmental catalyst. The material was designed and visualized using computerized programme. The sample was then prepared by conventional solid state reaction method for its applications. A very little work has been reported for  $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}$  phosphor and especially no work has been found for the TL properties of Oxygen ion beam irradiated synthesized samples. Moreover in the current era of research radiation dosimetry heavy ion beam is gaining lot of importance. So, in the light of literature survey, the present work is focused on thermoluminescence properties of aluminosilicates,  $\text{NaAlSi}_2\text{O}_6$ : Dy and  $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}$ : Eu after irradiating the samples with 75 MeV  $\text{O}^{6+}$  ion beam for their applications in radiation dosimetry.

## 2. Experimental

$\text{NaAlSi}_2\text{O}_6$ : Dy was synthesized using Combustion method and is reported earlier by our group [20].  $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}$ : Eu<sup>3+</sup> phosphor was also prepared using the starting materials  $\text{NaNO}_3$ , Al ( $\text{NO}_3$ )<sub>3</sub>,  $\text{SiO}_2$ ,  $\text{NH}_2\text{-CO-NH}_2$  in the stoichiometric ratio 6:6:10.  $\text{NH}_2\text{-CO-NH}_2$  acted as fuel for combustion and rare earth element Europium oxide is used as doping agent, after dissolving in Nitric Acid. All the materials were mixed and crushed together in a pestle mortar to form homogeneous liquid mixture that was heated in muffle furnace preheated at 550 °C. The mixture produced flameless combustion to form required phosphor in the powder form. The

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## Synthesis and optical properties of innovative degradable black pepper composite material

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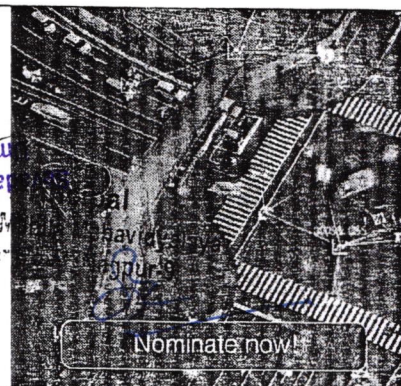
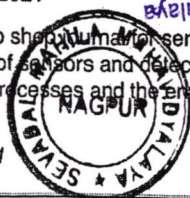


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## Synthesis and optical properties of innovative degradable black pepper composite material

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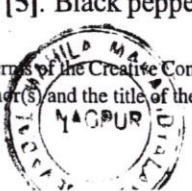
**Abstract.** Widely used as a medicinal plant in Ayurveda black pepper is also a main content of spices. Easily available of such kind of herb is studied the first time as a luminescence point of view. In this paper, we have studied luminescence characteristics of black pepper samples and check their properties for LED applications which are synthesized in four parts 1) Pure powder of black pepper 2) Black Pepper Solution by ethanol 3) Europium (Eu) doped black pepper solution and 4) Black Pepper thin film. The synthesized samples were characterized by Photoluminescence (PL) techniques. The PL characteristics for all four samples showed interesting results. Pure black pepper powder showed PL emission at 471nm under 421nm excitation wavelength. Black pepper solution shows an emission band around 430nm under 397nm excitation. Europium doped black pepper solution shows two emission peaks at 516nm and 658nm under 440nm excitation wavelength. Thin-film of pure black pepper shows an emission band around 454nm under 390nm excitation wavelength. The CIE Chromaticity Coordinates of the Black Pepper and other synthesized samples shows color co-ordinates near the blue and white region in the visible spectrum. These CIE chromaticity co-ordinates demonstrate high spectral characterization of developed materials such as high color purity and excellent chromaticity co-ordinates. The entire photoluminescence results indicated that synthesized samples have promising potential for LED applications.

**Keywords:** Black Pepper; degradable; Photoluminescence; LED

### 1. Introduction

In the last decades, white light-emitting diodes (WLEDs) have attracted the special attention of research society, people, researchers and currently it has become the most promising lighting device [1]. Incredibly, WLEDs will be used more widely in the coming generation and will lead to a new phosphor research program, because they have marvelous advantages such as high brightness, good reliability, fast response, environmental friendliness, long operating lifetime, low electricity consumption, etc [1, 2]. In the current scenario, numerous researchers and scholars are working in the field of luminescence, and they have paid more attention towards the synthesis and characterization of luminescent materials because it is widely used for various application such as field emission displays (FED) solid-state laser media, infrared to-visible up-converters, Solid state lighting, Solar Cell fiber amplifiers, etc [3, 4].

In the present study, black pepper material were studied for study of luminescence properties, that study revealed pepper family is one of the best families that showing enormous potential in the field of luminescence, it is also known as Piperaceae [5]. Black pepper is easily available and most commonly





## Photoluminescence study of $\text{Ce}^{3+}$ activated blue emitting $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}$ lamp phosphors

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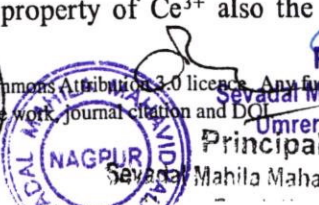
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**Abstract.** The photoluminescence analytical study of  $\text{Ce}^{3+}$  doped  $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}$  phosphors is done in this research work. Powder X-ray diffraction technique (XRD) along with scanning electron microscope i.e. (SEM), CIE colour coordinates including their PL properties with emission intensity effect too were analyzed for the characteristics of prepared phosphors. In the instance of  $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:\text{Ce}^{3+}$ , the emission spectra demonstrates an exclusive 442 nm centered band corresponding to  $\text{Ce}^{3+}$ 's 4f-5d transition. The result specifies that the  $\text{Ce}^{3+}$  activated  $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}$  phosphor could find out applications in the light phosphor production.

**Keyword:** -Photoluminescence, XRD, SEM, CIE,

### 1. Introduction

Synthetic alkaline rare earth aluminates enabled by  $\text{Ce}^{3+}$  ions are professional luminescence compounds, exhibiting a blue emission marked by excellent quantum output under UV excitation [1]. They are commonly used in PDPs, field emission displays (FEDs), and fluorescence lamps [2, 3]. The solid-state reaction process usually produces alkaline earth aluminate phosphors. Combustion synthesis is a new method introduced to the production of phosphor over the last few years [4]. Synthesis of the combustion involves an exothermic reaction among metal nitrates and a fuel. This method creates the as-synthesized state of strongly crystalline powders. Within this paper the specimen of the  $\text{Ce}^{3+}$  co-doped  $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}$  were synthesized through an easy process of combustion. We investigated their emission and excitation spectra, and identified a blue afterglow. The effectiveness in luminescence can be significantly improved when phosphors are doped with appropriate supplementary activators [5]. Owing to  $\text{Ce}^{3+}$ 's strong spectroscopic properties and its aptitude to integrate  $\text{Ce}^{3+}$  ion into a lot of unique host resources,  $\text{Ce}^{3+}$  enabled components have created increasing interest in a variety of applications. [6]. These all-prepared materials incorporate greater returns, emission wavelength with adequate reaction, rapid luminosity decreases in testing and stable temperatures, rendering them desirable for use in high energy branch of physics study [4] as well as in medicinal imaging applications [5]. On the basis of outstanding luminescence properties, inorganic activated  $\text{Ce}^{3+}$  materials are therefore used for ionizing radiation in displays, lighting systems and certain other applications. [7].  $\text{Ce}^{3+}$  can be sustained in the oxidation state of a host material. The luminescence inquiries studied and checked the stability and incorporation of Ce ions into the sample. For the reason that positive spectroscopic property of  $\text{Ce}^{3+}$  also the potential to



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## Synthesis and photoluminescence properties of novel red-emitting $\text{KMg}_4(\text{PO}_4)_3: \text{Eu}^{3+}$ phosphors for UV- excited white-light emitting diodes

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**Abstract.** The trivalent  $\text{Eu}^{3+}$  activated  $\text{KMg}_4(\text{PO}_4)_3$  phosphor has been successfully prepared via solid state diffusion technique. The phase formation and structural morphological studies carried out by XRD pattern and SEM analysis. The photoluminescence excitation spectra centred at 395 nm attributed to  $^7\text{F}_0 \rightarrow ^5\text{L}_6$  energy transition levels. PL emission spectra centred at 593 nm and 613 nm corresponds to  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  ( $J=1,2$ ) transitions of  $\text{Eu}^{3+}$  in the host respectively. The experimental results showed that  $\text{Eu}^{3+}$  singly doped  $\text{KMg}_4(\text{PO}_4)_3$  phosphor under UV excitation gives intense red emissions. The critical  $\text{Eu}^{3+}$  quenching concentration (QC) was determined to be 1.0 mol% along with excellent CIE coordinates of (0.6326, 0.3670). All the above results exhibits, the prepared phosphor is promising material as UV excitable red emitting phosphor for w-LED.

**Keywords:** Phosphor; Down conversion; Luminescence; Chromaticity coordinates; W-LEDs

### 1. Introduction

In the recent year trivalent rare-earth ( $\text{RE}^{3+}$ ) ions doped inorganic based phosphor received more attention as luminescent materials owing to their wide application in the various field such as w-LEDs, medical applications, non-inversion thermometry, solar energy conversion, temperature sensors, field emission displays and solid state lighting (SSL), due to existence of emissions attributes to electronic transitions in the  $4f_n$  configurations [1–3]. In the present era energy saving is the prime issue and hence major inclination towards w-LEDs in display technology owing to its excellent performance, low power consumption, durability, high compatibility, energy saving, as well as are of highly economical [4,5]. In order to realize the excellent luminescent materials, it must exhibits some important characteristics such as prominent emission efficiency under n-UV/blue excitation, good thermal and chemical stability as well as narrow band emission with good absorption. In general two approach are adopted to achieve pc-w-LEDs include (i) combination of yellow emitting ( $\text{YAG}:\text{Ce}^{3+}$ ) phosphor with blue emitting ( $\text{InGaN}$ ) chip but owing to lack of red emission it shows high CCT and poor CRI which hinder its commerce alization. (ii) This limitation can be overcome with the approach of combination of RGB phosphor with n-UV or blue excitation chip to improve the optical properties [6]. The poor thermal stabilities and aging rates of the different phosphors also restrict their applications in w-LEDs [7,8]. Moreover, various components of inorganic luminescent phosphor materials encompass with borates [9], Aluminate [10], vanadates [11], tungstates [12], silicates [13] and phosphates [14] have been studied for generation of



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## Recent progress in phosphate based luminescent materials: A case study

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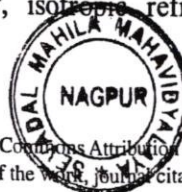
**Abstract.** The uses of phosphate based luminescent materials are presented in this study in different fields of luminescence. There are different types of luminescent phosphors available in the field of luminescence such as borates, sulphates, fluorides, sulphides, phosphates etc. From all these phosphors, phosphate-based phosphors show their potential in almost every field of luminescence in last few years and it becomes a key material in the luminescence especially in photoluminescence, thermoluminescence and mechanoluminescence. These rare earths activated phosphate-based luminescence materials are synthesized with different techniques by means of wet chemical method, combustion technique, sol gel analysis and solid-state diffusion technique etc. which are described in the present article. Consequently, this article chiefly dealing the overview of different phosphate based luminescent materials and modern development and progression in the field of luminescence.

**Keywords:** phosphates; luminescent materials; chemical synthesis; dosimetry; photoluminescence.

### 1. Introduction

Luminescence phenomenon is essentially known for the emission of cold light from the different energy sources which take place at the comparatively low temperatures [1]. Some energy source transferred to an electron from ground to excited state, and then the energy releases by the electron in the form of light so it can fall back to its ground state in luminescence phenomenon. Luminescent material is also called 'phosphors'. Phosphors are consisting of a host lattice and a luminescent center frequently known as an "Activator". The activators absorb the exciting radiations and are elevated to an excited state. The excited state proceeds for the ground state by release of radiation. The activator does not absorb the excitation radiation in several materials although the erstwhile ion might absorb the exciting radiation and then move it to the activator. In such studies the absorbing ion is known to be a sensitizer [2]. In various cases the host lattice transmits the excitation energy to the activator, thus the host lattice function as a "Sensitizer". The host lattice is comprised of as a minimum one sort of oxide obtained from the sulphide [3], aluminate [4,5], aluminosilicate [6], silicate [7], titanate [8], niobate [9], phosphate [10], halophosphate [11], Borate [11], tungstate [12] etc.

Above all the materials, phosphate plays a significant role in environmental systems and utilize a wide range of functions in consequence of their outstanding simplicity, low viscosity, high ultraviolet (UV) transmission, high-quality mechanical, thermal constancy, isotropic refractive index and simple



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## Combustion synthesis and spectroscopic properties of $\text{Ba}_2\text{Zn}_x\text{F}_{18}:\text{Eu}^{3+}$ phosphor

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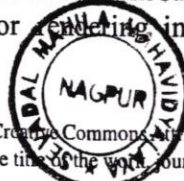
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**Abstract.** In the present work, a series of  $\text{Ba}_{2-x}\text{Zn}_x\text{F}_{18}:\text{Eu}^{3+}$  ( $x = 0.1, 0.5, 0.7, 1.0, 1.5$ ) phosphors were synthesized by combustion method. The spectroscopic properties of synthesized phosphor were observed by photoluminescence and photometric characterization technique. The observed excitation spectra revealed two bands around 395nm and 466nm that was attributed to the  $^7\text{F}_0 \rightarrow ^5\text{L}_6$ , and  $^7\text{F}_0 \rightarrow ^5\text{D}_2$ , transition of trivalent europium ions, respectively. Under 395nm and 466nm excitation, the PL emission spectra shows several emission bands around at 580nm, 593nm and 613nm, which are ascribed due to  $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_1$ , and  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition of  $\text{Eu}^{3+}$  ions, respectively. The emission band of 613nm indicates the highest emission intensity compared to the other emission bands. The emission band revealed the highest emission intensity at 1mol% concentration of  $\text{Eu}^{3+}$  ions. Further, a CIE chromaticity diagram was obtained, which is confirmed that red emission. The entire investigation and their outcomes revealed that the synthesized phosphors exhibit strong red emission, which can be applied in the lighting industry and display applications.

**Keywords:** Combustion method; Photoluminescence; CIE Coordinate

### 1. Introduction

In the current scenario, rare earth activated luminescent materials have attract more attention due to their advantages and applicability in various fields such as solid-state lighting, display devices, solar cell, TLD badges, fingerprint detection, plant growth, temperature sensor, medical applications, etc [1–4]. White LEDs are novel lighting technology in field of lighting applications. In the last few years, phosphor converted-WLEDs has grown popularity and it is already used commercially in various applications such as traffic lights, outdoor lighting, inside and outside lighting in airplane, vehicles, and transports, etc [5–7]. Due to their popularity, WLEDs will be utilized more broadly in the coming years and will prompt the development of new novel materials for commercial lighting. WLEDs can reduce energy dissipation in the field of lighting. Generally three ways are known for white light generation based on LEDs (i) yellow-emitting phosphor excited by blue-emitting diode (ii) combination of Red, Green and Blue (RGB) LED lights and (iii) By combination of RGB phosphor with near UV LEDs [8,9]. A combination of yellow emitting (YAG:  $\text{Ce}^{3+}$ ) phosphors with a blue emission (InGaN) chip is used as commercial WLEDs, but this method faces some drawbacks such as lack of red emission, high correlated color temperature (CCT), and poor color rendering index (CRI), which hinders its



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## Photoluminescence properties of wet-chemically synthesized $Tb^{3+}$ and $Sm^{3+}$ doped $K_3Ca_2(SO_4)_3Cl$ phosphor

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**Abstract.** In this study, we are successfully synthesized terbium and samarium ( $Tb^{3+}/Sm^{3+}$ ) doped  $K_3Ca_2(SO_4)_3Cl$  phosphors by wet chemical method, and synthesized phosphors were characterized by XRD, SEM, and Photoluminescence (PL) techniques, and studied in detail. Photoluminescence analysis, we can see that under the Near-UV (NUV) excitation of 380nm, the  $Tb^{3+}$  activated samples showed a prominent green emission peak at 546nm attributed to the  $^5D_4 \rightarrow ^7F_5$  transition of  $Tb^{3+}$  ions. While the PL emission spectra of 404 nm light excited  $K_3Ca_2(SO_4)_3Cl:Sm^{3+}$  phosphors showed three emission lines at 565nm, 598nm and 645nm attributed to  $^4G_{5/2} \rightarrow ^6H_{5/2}$ ,  $^4G_{5/2} \rightarrow ^6H_{7/2}$ , and  $^4G_{5/2} \rightarrow ^6H_{9/2}$  transitions of  $Sm^{3+}$  ions, respectively. The CIE coordinates were calculated to be (0.263, 0.515) for  $K_3Ca_2(SO_4)_3Cl:Tb^{3+}$  and (0.532, 0.462) for  $K_3Ca_2(SO_4)_3Cl:1.5mol\%Sm^{3+}$ , which lied in the green and orange regions, respectively. The entire photoluminescence results indicated that phosphor  $K_3Ca_2(SO_4)_3Cl$  doped with  $Tb^{3+}$  and  $Sm^{3+}$  may turn out to be an important component of pc-white LEDs and display devices.

**Key words.** Wet chemical method; SEM; XRD; pc-white LEDs; lamp phosphor.

### 1. Introduction

In the last few years, lanthanide ion doped phosphor materials have attracted a lot of attention of the society, because in these years, rare earth activated phosphors has proved its utility in various applications such as optical communications, X-ray imaging, cathode ray tubes, biological labelling, lasers, white light-emitting devices (WLEDs), optoelectronic devices, vacuum fluorescent display, etc [1–3]. Presently, phosphors converted light emitting diode (PC-LED) has brought an industrial revolution in the field of lighting and has gained a lot of public acclaim due to its high-quality properties. It is the latest technology in the field of lighting, which has a tremendous market share. Currently, PC-LEDs have proved his capabilities for replacing traditional incandescent light bulb because PC-LEDs has extraordinary features such as compact size, high luminous efficiency, energy saving, long operation life, environmentally friendly nature [4–8]. Recently, the phosphor converted LED-based white light sources have gained enormous research interest due to their high applicability in indoor and outdoor lighting technology. The most widely used white LEDs are composed of InGaN-based blue-LED chip coupled with YAG:Ce<sup>3+</sup> yellow phosphor [9]. However, this technique has also revealed some drawbacks such as the lack of a red component, low color rendering index (CRI), high correlated color temperature (CCT). As a supplementary method, red, blue, and green-emitting phosphors are excited by ultraviolet (UV) or near-UV (NUV) LEDs. The light obtained by this method provides high quality light with better color stability and high color



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## Wavelength down-conversion study of $\text{Ba}_3\text{Y}_{1-x}(\text{BO}_3)_3: x\text{Tb}^{3+} \& \text{Eu}^{3+}$ [ $0.005 \leq x \leq 0.05$ ] phosphor for solid state lighting applications

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**Abstract.** In this work, we synthesized the  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  doped  $\alpha\text{-Ba}_3\text{Y}(\text{BO}_3)_3$  phosphor using the solution combustion method. Using the powder XRD pattern and FTIR low-temperature phase of  $\alpha\text{-Ba}_3\text{Y}_{1-x}(\text{BO}_3)_3: x\text{Tb}^{3+} \& \text{Eu}^{3+}$  was confirmed. Element composition with percentage was verified by FE-SEM-EDS. Stoke's shift values were calculated which confirms the high thermal stability of the phosphor & its use in high power WLED. Photoluminescence study at room temperature was done. Intrinsic absorption due to the 4f-4f transition of  $\text{Eu}^{3+}$  results intense red emission from  $\alpha\text{-Ba}_3\text{Y}_{1-x}(\text{BO}_3)_3: x\text{Eu}^{3+}$  makes it suitable for pc-WLED and confirms the Centro-inversion symmetry site of  $\text{Eu}^{3+}$  in the host. Green emission at NUV excitation from  $\text{Ba}_3\text{Y}_{1-x}(\text{BO}_3)_3: x\text{Tb}^{3+}$  results from cross-relaxation of  $\text{Tb}^{3+}$  in a host. The concentration quenching reason for both activators was investigated by calculating and comparing critical distance. The purity of luminescence color was confirmed by plotting CIE-chromaticity co-ordinates on CIE-Color gamut. The entire work confirms the importance of synthesized phosphor along with previously reported same host materials. The reported phosphor may be suitable for NUV converted WLED, wavelength conversion devices, and high power RGB - WLED.

**Keywords:** Solution combustion, Borate Phosphors, Terbium, Europium, Photo-luminescence.

**1. Introduction:** Inorganic phosphors based WLED are widely used because of properties like energy efficiency, lifetime, stability, Cost-effective, design and ecofriendly nature. Inorganic luminescent materials have considerable importance in fluorescent lamps, solid-state lighting, phosphorescent paints, in road marking paints, high power LED etc. Wavelength conversion and color mixing are the most commonly used technology to produce white light [1-6]. So, the development of efficient phosphors for the wide possible applications is the favorite research area of material science. Abundant energy levels and the large number of possible transitions in the visible/UV light region makes the rare earths most common dopants in synthesis of borate phosphors [7]. Among Rare earth ion,  $\text{Tb}^{3+}$  is one of the most prospective green-emitting activators due to its 4f-4f transitions and  $\text{Eu}^{3+}$  is the promising red-emitting activator dopant [8].

The borate compound with formula  $\text{M}_3\text{Ln}(\text{BO}_3)_3$  ( $\text{M} = \text{Ba}, \text{Sr}$ , and  $\text{Ln} = \text{La-Lu}, \text{Y}, \text{Sc}$ ) were reported as promising phosphors for W-LED applications. The  $\text{Ba}_3\text{Y}(\text{BO}_3)_3$  crystal exists in two structures, i.e., low-temperature phase  $\alpha\text{-Ba}_3\text{Y}(\text{BO}_3)_3$  with space group  $\text{P}6_3\text{cm}$  and high-temperature phase  $\beta\text{-Ba}_3\text{Y}(\text{BO}_3)_3$  with space group  $\text{R}3$ . The photoluminescence properties under doping are different for both phases. The structure of  $\alpha\text{-Ba}_3\text{Y}(\text{BO}_3)_3$  consists of 3-F-C boron atoms, 6-F-C yttrium atoms, 9 & 6-F-C barium atoms [9]. Irish Valerie et.al synthesized the  $\text{Ba}_3\text{Y}(\text{BO}_3)_3: \text{Eu}^{3+}, \text{Bi}^{3+}$  phosphor via a solid-state reaction and studied it as a phosphor for w-LEDs using N-UV LED chips [10]. Xiulan Wu et.al. described  $\text{Ba}_3\text{Y}(\text{BO}_3)_3: \text{Sm}^{3+}$  as orange-red phosphor for WLEDs [11]. Jingjie Yu et.al. investigated luminescent and the



  
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# Wet chemically prepared terbium activated sodium calcium chlorosulfate phosphor for solid state lighting industry

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## ABSTRACT

Rare earth ion plays an important role in the solid state lighting industry. Here, the terbium (III) ion doped sodium calcium chlorosulfate phosphor was prepared via wet chemical method. Structure, bonding between each element of the sample and morphology of the sample were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM), which showed that the samples were crystallized in a well known structure. XRD study shows the crystalline nature of the phosphor materials prepared at low temperature. Photoluminescence study of prepared phosphor was done using SHIMADZU Spectrofluorophotometer RF-5301 PC with a xenon lamp as the excitation source. The excitation spectra are obtained between 280 and 430 nm ranges on doping of terbium (III) ion. Among all these transitions excitation at 380 nm is strong excitation owing to  $^7F_6 \rightarrow ^5G_6$  transition. The emissions from terbium (III) ions are at 416, 437, 490 and 545, 586, 621 nm. These emissions are attributed to  $^5D_3 \rightarrow ^7F_5$  (417 nm),  $^5D_3 \rightarrow ^7F_4$  (437 nm),  $^5D_4 \rightarrow ^7F_6$  (491 nm) and  $^5D_4 \rightarrow ^7F_5$  (545 nm),  $^5D_4 \rightarrow ^7F_4$  (588 nm),  $^5D_4 \rightarrow ^7F_3$  (624 nm) transitions of terbium (III) ions. Among these strong emission peak appears in green region at 545 nm.

## ARTICLE HISTORY

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## KEYWORDS

Solid state lighting; lamp phosphor; rare earth ion; LEDs; photoluminescence


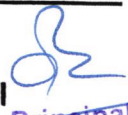
## 1. Introduction

Rare earth doped sulfate materials have been widely investigated because of the varied optical energy level structures of the rare earth elements which result in light emission from ultraviolet to far-infrared regions (1–5). Until now, several complex oxides, for instance silicates (6), aluminates (7) and borates (8), which have strong absorption in the VUV range, have been deliberated. Stoichiometric rare earth sulfates have gained a special attention because of their interesting physical properties, such as optical properties (9, 10). Imitation alkaline earth fluoride-sulfates doped by divalent europium and trivalent dysprosium are efficient photo luminescent materials. The europium activated phosphor is used as blue component in three band fluorescent lamps, light-emitting diodes (LED) (11–13) and dysprosium doped phosphors are used as tricolor component in fluorescent lamps and white

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## REVIEW

# Short review on recent progress in $\text{Mn}^{4+}$ -activated oxide phosphors for indoor plant light-emitting diodes

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## Abstract

In the modern era, growing number of indoor plants for various purposes, such as vegetation, flowering, and decorations, has increased over the traditional follow-up trends for plantation. However, the indoor plantation requires different parameters for their growth; among these, light plays a significant role. In order to control the growth of plants using light-emitting diodes, Mn-doped oxide phosphors have emerged as promising candidates due to their broad and intense emission bands in the red and far-red spectral range. In this review article, recent progress on Mn-doped oxides for indoor plant growth has been reviewed. This review article is mainly divided into three parts. In the first part, different reaction conditions for the synthesis of Mn-doped oxide phosphors are compared. In the second part, the luminescent and other photometric parameters of these are discussed. The influence of different co-dopants on the luminescent characteristics has been elucidated in detail. The third part discusses the properties of light-emitting diodes fabricated using these phosphors for plant growth. The present review article elucidates the synthesis parameters, luminescent properties, and light-emitting diodes fabricated using Mn-doped oxide materials for plant growth applications.

## KEYWORDS

co-doping, doping, light-emitting diodes, Mn, oxides, plant cultivation

## 1 | INTRODUCTION

In the present era, the trend of growing plants through horticulture has revolutionized owing to its benefits over the traditional agricultural methods. The horticulture includes the growing of plants, flowers, and other vegetables under specific weather conditions (e.g., light, air, water, temperature).<sup>[1–4]</sup> It also overcomes the problems encountered due to natural calamities such as flood, drought, typhoons, hail, and haze. Among the various factors for plant growth, light has a pivotal role. We all know that the natural source of light for plants is sunlight.<sup>[5–7]</sup> Sunlight has a wide spectrum of radiations ranging from visible light to infrared (IR) necessary for plant growth. There are mainly four pigments in the plants, namely, chlorophyll a and b absorb in the blue region, phytochrome  $P_R$  absorbs in the red (R) region, and phytochrome  $P_{FR}$  absorbs in the far-red (FR) region.

The blue, red, and FR lights help in plant growth via different mechanisms such as phototropic, photosynthesis, and photomorphogenesis processes.<sup>[8–15]</sup> In addition to this, there is shade avoidance syndrome in plants, exhibited by variation in the concentration of phytochrome  $P_R$  and  $P_{FR}$ .<sup>[8]</sup> The concentration of these two phytochromes is affected by the variation in the intensity of the R to FR ratio. It is reported that the intensity ratio of R and FR in daylight is 1.15 and varies with climatic conditions. In the dark, phytochrome ( $P_R$ ) is synthesized by absorbing red light around 660 nm.  $P_R$  is generally considered biologically inactive, while  $P_{FR}$  is biologically active, and activity is acquired upon absorbing in the FR region around 730 nm. The phytochromes will translate the relative amounts of R and FR light in incident radiation into different relative concentrations of the active  $P_{FR}$  form of phytochrome. The shade avoidance response is found in the plants when there is a limit in the lighting. The reduction in the  $P_{FR}$



# LUMINESCENCE

The Journal of Biological and Chemical Luminescence



SPECIAL ISSUE ARTICLE

## Thermoluminescence dosimetry properties and kinetic analysis of $K_3Ca_2(SO_4)_3F:Dy^{3+}$ phosphor

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## RESEARCH ARTICLE

Solid state diffusion and amalgamating anionic exchange at a  $\text{KNaSO}_4$  phosphors activated with  $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$  and  $\text{Sm}^{3+}$  rare earth ions to enhance w-LED performanceArati Duragkar<sup>1</sup> | Nirupama S. Dhoble<sup>1</sup> | Ritesh L. Kohale<sup>2</sup> | Sanjay J. Dhoble<sup>3</sup><sup>1</sup>Department of Chemistry, Sevalal Mahila Mahavidyalaya, Nagpur, India<sup>2</sup>Department of Physics, Sant Gadge Maharaj Mahavidyalaya, Hingna, Nagpur, India<sup>3</sup>Department of Physics, R.T.M. Nagpur University, Nagpur, India

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## Abstract

In present work,  $\text{KNa}(\text{SO}_4)$  phosphors doped with different concentrations of rare earth  $\text{Eu}^{3+}$ ,  $\text{Sm}^{3+}$  and  $\text{Dy}^{3+}$  ions (0.05, 0.1, 0.3, 0.5, 0.7, 1 mol%) were synthesized using a solid-state diffusion technique. Photoluminescence (PL) investigations were carried out for the whole range of  $\text{Eu}^{3+}$ ,  $\text{Sm}^{3+}$  and  $\text{Dy}^{3+}$ -doped phosphors; rare earth ions that retained maximum PL intensity were selected for advanced anionic exchange. In the present investigation, phosphors  $\text{KNa}(\text{SO}_4):\text{Eu}^{3+}$  (1 mol%),  $\text{KNa}(\text{SO}_4):\text{Dy}^{3+}$  (0.5 mol%) and  $\text{KNa}(\text{SO}_4):\text{Sm}^{3+}$  (0.3 mol%) had the highest PL intensity, and were therefore selected for further anionic substitution of sulphate anions with different concentrations of vanadate, phosphate, and tungstate anions, such as  $\text{KNa}(\text{SO}_4)_{1-x}(\text{MO}_4)_x$ : W (where W =  $\text{Eu}^{3+}$  1 mol%,  $\text{Dy}^{3+}$  0.5 mol% and  $\text{Sm}^{3+}$  0.3 mol%;  $\text{MO}_4 = \text{PO}_4$ ,  $\text{VO}_4$ ,  $\text{WO}_4$ ; and x = 0.1, 0.3, 0.5, 0.7, 1). Structural and molecular environments of the substituted phosphors were characterized individually using X-ray diffraction and Fourier transform infrared spectroscopy. In-depth morphological investigations of the prepared phosphors were undertaken using scanning electron microscopy. For the principal investigation on enhancement of white light-emitting diode (w-LED) performance, the PL properties of all the synthesized phosphors were studied analytically. Emission intensity ratios for  $\text{KNa}(\text{SO}_4):\text{Eu}^{3+}$  1 mol%,  $\text{KNa}(\text{SO}_4)_0(\text{PO}_4)_1:\text{Eu}$  1 mol%,  $\text{KNa}(\text{SO}_4)_{0.9}(\text{VO}_4)_{0.1}:\text{Eu}$  1 mol%, and  $\text{KNa}(\text{SO}_4)_{0.9}(\text{WO}_4)_{0.1}:\text{Eu}$  1 mol% were 1:1.15:1.23:0.08. PL intensity ratios for the phosphors  $\text{KNaSO}_4:\text{Dy}$  0.5 mol% and  $\text{KNa}(\text{SO}_4)_{0.9}(\text{PO}_4)_{0.1}:\text{Dy}$  0.5 mol% was 1:2. The ratio of PL intensity was 1:3.2:0.8 for  $\text{KNa}(\text{SO}_4):\text{Sm}$  1 mol%,  $\text{KNa}(\text{SO}_4)_{0.5}(\text{PO}_4)_{0.5}:\text{Sm}$  0.3 mol%, and  $\text{KNa}(\text{SO}_4)_{0.7}(\text{VO}_4)_{0.3}:\text{Sm}$  0.3 mol% phosphors, respectively. Chromaticity investigations were carried out using Commission Internationale de l'Éclairage colour co-ordinate diagrams, which suggested that the prepared  $\text{Eu}^{3+}$ -doped and  $\text{Sm}^{3+}$ -doped phosphors would be prospective candidates for red and green LEDs, respectively, whereas  $\text{Dy}^{3+}$ -doped phosphors showed emission in the blue and yellow regions. The entire study indicated that amalgamation of anionic exchange at a  $\text{KNaSO}_4$  phosphor activated with  $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$  and  $\text{Sm}^{3+}$  rare earth ions could generate and enhance white light emission.



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PATENT APPLICATION PUBLICATION

INDIA

Date of filing of Application :23/05/2019

(21) Application No.201921020429 A

(43) Publication Date : 25/10/2019

Title of the invention : METHOD FOR THE SYNTHESIS OF DEGRADABLE BLACK PEPPER COMPOSITE MATERIAL

International classification :G02B11/16  
Priority Document No :NA  
Priority Date :NA  
Name of priority country :NA  
International Application No :NA  
Filing Date :NA  
International Publication No :NA  
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Filing Date :NA  
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Filing Date :NA

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(73) Abstract :

Present invention relates to a method for the synthesis of degradable black pepper composite material for LED application. The object of the proposed invention is to provide eco-friendly and degradable luminescent material to apply in light emitting diodes (LED) and display devices. The proposed methodology divides in four parts; 1) Pure powder of black pepper 2) Black Pepper Solution by ethanol 3) Europium(Eu) doped black pepper solution and 4) Black Pepper thin film. All these parts are characterized by Photoluminescence (PL). PL characteristics in all parts showed interesting results. Following invention is described in detail with the help of Figure 1 of sheet 1 showing PL Excitation spectra of black pepper powder at  $\lambda_{em}=464nm$ , Figure 2 of sheet 1 showing PL Emission of black pepper powder at  $\lambda_{ex}=380nm$  and Figure 3 of sheet 2 showing PL Emission of black pepper powder at  $\lambda_{ex}=421nm$ . Figure 10 of sheet 6 showing PL emission of black pepper composite with Eu at 516 nm and 658nm at  $\lambda_{ex} = 440nm$ .

No. of Pages : 23 No. of Claims : 1

The Patent Office Journal No. 43/2019 Dated 25/10/2019

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# INTERNATIONAL APPLICATION PUBLICATION

(21) Application No.201921008367 A

Date of Filing of Application :04/03/2019

(43) Publication Date : 17/05/2019

Title of the Invention : GAMMA RADIATION SHIELDING COMPOSITE MATERIALS

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Priority Date	:NA	(72)Name of Inventor :
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International Application No	:NA	2)Dr. Anup P. Bhat
Filing Date	:NA	3)Mrs. Swati V. Joshi
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Point of Addition to Application Number	:NA	5)Dr. Prashant Bokare
Filing Date	:NA	6)Dr. Nirupama S. Dhoble
Point of Addition to Application Number	:NA	
Filing Date	:NA	

**Abstract :**  
 Present invention relates to a gamma radiation shielding composite materials with placement techniques of fly ash bricks. The present invention pertains to multi-component composite materials and techniques that provide improved capabilities for shielding against penetrating, harmful neutron and gamma radiation, as well as alpha and beta radiation emitted by high-level, transuranic and radioactive wastes. These radiation shielding composite materials offer better capacity for shielding of high flux neutron and gamma radiation. In addition, cooling of fly ash surfaces is required during radioactive waste storage to further the length of the of fly ash and high radioactive temperature, and more cost-effective shielding capabilities than those of the conventional of fly ash, lead and steel shields. Following invention is described in detail with the help of Figure 1 of sheet 1 showing computational synthesis flow chart and Figure 2 of sheet 2 showing block diagram of measurement system.

Number of Pages : 21 No. of Claims : 10

The Patent Office Journal No. 20/2019 Date: 17/05/2019



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(12) PATENT APPLICATION PUBLICATION

(19) INDIA

(22) Date of filing of Application : 07/05/2020

(21) Application No. 202021019460 A

(43) Publication Date : 03/07/2020

(54) Title of the invention : A SYNTHESIS OF  $\text{CaAl}_2\text{Si}_4\text{O}_{12}:\text{Dy}_3$ +BLUE PHOSPHOR FOR LED APPLICATION

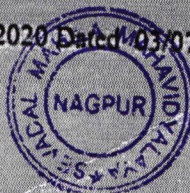
(51) International classification	:C09K0011770000, H01L0033500000, C09K0011080000, C23C0014060000, H01J0011420000	(71) Name of Applicant : 1) Chaitali M. Mehare Address of Applicant : Department of Physics, R.T.M. Nagpur University, Nagpur-440033, India Maharashtra India 2) Renu Nayar 3) Nirupama S. Dhoble 4) Sanjay J. Dhoble
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(32) Priority Date	:NA	
(33) Name of priority country	:NA	
(36) International Application No	:NA	
Filing Date	:NA	
(37) International Publication No	:NA	
(38) Patent of Addition to Application Number	:NA	
Filing Date	:NA	
(42) Divisional to Application Number	:NA	
Filing Date	:NA	

(57) Abstract :

The present invention relates to a process for the synthesis of blue phosphor for LED application. The object is to provide a process for synthesis of novel  $\text{CaAl}_2\text{Si}_4\text{O}_{12}:\text{Dy}_3$ +blue phosphor by using combustion method. The formation of crystal structure and surface morphology is analyzed by X-ray diffraction pattern and scanning electron microscopy techniques. The photoluminescence analysis reveals that prepared phosphor material exhibits an excellent emission at 422 nm, with two peaks around 479 nm and 575 nm monitor at excitation wavelength of near UV 369 nm. In addition, CIE color chromaticity confirms the emission colors locate at the blue light region. This blue emission supports the UV-excited white LED as a one of the candidate of blue emitting material. Following invention is described in detail with the help of Figure 1 of sheet 1 showing flow chart for synthesis  $\text{CaAl}_2\text{Si}_4\text{O}_{12}:\text{xDy}_3$ + (0.05 x 7.0 mole%) phosphor by combustion method.

No. of Pages : 17 No. of Claims : 2

The Patent Office Journal No. 27/2020 Dated 03/07/2020



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(12) PATENT APPLICATION PUBLICATION

(21) Application No. 202021019718 A

(19) INDIA

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(43) Publication Date : 03/07/2020

(54) Title of the invention : A MORTUARY CABINET FOR DISINFECTION OF VIRUS INFECTED DEAD BODIES

(51) International classification	:A61G0017060000, A61L0002100000, A01N0001000000, C02F0001320000, A61L0002180000	(71) Name of Applicant : 1) Niles M. Mahajan Address of Applicant : Department of Pharmaceutics, Dadasaheb Balpande College of Pharmacy, Nagpur- 440037, MS, India Maharashtra India 2) Nirupama S. Dhoble 3) Sanjay J. Dhoble
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(32) Priority Date	:NA	
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(86) International Application No	:NA	
Filing Date	:NA	
(87) International Publication No	:NA	
(61) Patent of Addition to Application Number	:NA	
Filing Date	:NA	
(62) Divisional to Application Number	:NA	
Filing Date	:NA	

(57) Abstract :

The present invention relates to a mortuary cabinet for disinfection of virus infected dead bodies. The object of the proposed invention is to provide a sanitization cabinet using UV radiation for corona affected dismissal of dead body (3) for protecting the families and relatives from getting infected. The proposed unit has height, width and length as 4—4—7.5 ft3 respectively. All side wall of the cabinet is constructed by thick plastics. UVC lamp i.e. 200 nm to 280 nm wavelength are used for UV exposure purposed. UVC light crushed the NRA of virus and lamps with a radiation peak at around 254 nm for germicidal action for UV sensitization. Following invention is described in detail with the help of Figure 1 of sheet 1 showing the mortuary unit containing dead body (3) for UV radiation exposure, Figure 2 of sheet 1 showing mortuary unit containing dead body (3) wrapped in a plastic.

No. of Pages : 10 No. of Claims : 3

The Patent Office Journal No. 27/2020 Dated 03/07/2020



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(12) PATENT APPLICATION PUBLICATION

(19) INDIA

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(21) Application No. 202021034712 A

(43) Publication Date : 28/08/2020

(54) Title of the invention : A PROCESS FOR SYNTHESIS OF DEHYDRATED LUMINESCENT CHABAZITE PHOSPHOR

(51) International classification

:C06C

11/00

(31) Priority Document No

:NA

(32) Priority Date

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5) DHOBLE SANJAY J.

(57) Abstract :

The present invention relates to a process for synthesis of dehydrated luminescent chabazite phosphor. The object of the proposed invention is to provide a synthesis and characterization of Eu<sup>3+</sup> ion activated micro porous aluminosilicate Ca-chabazite Ca<sub>1.9</sub>Al<sub>3.8</sub>Si<sub>8.2</sub>O<sub>24</sub> phosphor. The chabazite phosphor has been synthesized using highly facile and robust combustion method. This method offers high temperature environment required for achieving highly pure and homogenous phosphor material with desirable properties. Hence the synthesis and assessment of electron vibrational interaction parameters find out its potential application in solid-state lighting. Following invention is described in detail with the help of Figure 1 of sheet 1 showing XRD graph of Ca<sub>1.9</sub>Al<sub>3.8</sub>Si<sub>8.2</sub>O<sub>24</sub>:Eu<sup>2+</sup> chabazite phosphor and Figure 2 of sheet 1 showing morphology of chabazite phosphor.

No. of Pages : 13 No. of Claims : 1

The Patent Office Journal No. 35/2020 Dated 28/08/2020



  
Principal

34693

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Australian Government  
IP Australia

# CERTIFICATE OF GRANT INNOVATION PATENT

Patent number: 2021102696

The Commissioner of Patents has granted the above patent on 23 June 2021, and certifies that the below particulars have been registered in the Register of Patents.

**Name and address of patentee(s):**

Abhijeet R. Kadam of Department of Physics, R.T.M. Nagpur University Nagpur 440033 India

Digambar A. Ovhal of Department of Physics, R.T.M. Nagpur University Nagpur 440033 India

Nirupama S. Dhoble of Department of Chemistry, Sevadal Mahila Mahavidhyalay Nagpur 440024 India

Sanjay J. Dhoble of Department of Physics, R.T.M. Nagpur University Nagpur 440033 India

**Title of invention:**

A SOLAR CELL EFFICIENCY ENHANCEMENT BY DOWNSHIFTING LAYER OF KALF4:DY3+, EU3+ CO-ACTIVATED DOWNCONVERSION PHOSPHOR AS SPECTRAL CONVERTERS

**Name of inventor(s):**

Kadam, Abhijeet R.; Ovhal, Digambar A.; Dhoble, Nirupama S. and Dhoble, Sanjay J.

**Term of Patent:**

Eight years from 19 May 2021

NOTE: This Innovation Patent cannot be enforced unless and until it has been examined by the Commissioner of Patents and a Certificate of Examination has been issued. See sections 120(1A) and 129A of the Patents Act 1990, set out on the reverse of this document.



Dated this 23<sup>rd</sup> day of June 2021

Commissioner of Patents

Principal

Sevadal Mahila Mahavidyalaya  
Ummer Road, Nagpur-9.

PATENTS ACT 1990







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# CERTIFICATE OF GRANT INNOVATION PATENT

Patent number: 2021102697

The Commissioner of Patents has granted the above patent on 23 June 2021, and certifies that the below particulars have been registered in the Register of Patents.

**Name and address of patentee(s):**

Yatish R. Parauha of Department of Physics, R.T.M. Nagpur University Nagpur 440033 India

Sonal P. Tatte of Department of Physics, R.T.M. Nagpur University Nagpur 440033 India

Nirupama S. Dhoble of Department of Chemistry, Sevadal Mahila Mahavidhyalay Nagpur 440024 India

Sanjay J. Dhoble of Department of Physics, R.T.M. Nagpur University Nagpur 440033 India

**Title of invention:**

A LOW-COST BLUE-EMITTING EU2+-ACTIVATED PHOSPHOR FOR NUV EXCITED WLEDs AND SOLAR CELL APPLICATIONS

**Name of inventor(s):**

Parauha, Yatish R.; Tatte, Sonal P.; Dhoble, Nirupama S. and Dhoble, Sanjay J.

**Term of Patent:**


Eight years from 19 May 2021

NOTE: This Innovation Patent cannot be enforced unless and until it has been examined by the Commissioner of Patents and a Certificate of Examination has been issued. See sections 120(1A) and 129A of the Patents Act 1990, set out on the reverse of this document.



Dated this 23<sup>rd</sup> day of June 2021

Commissioner of Patents

  
Principal

Sevadal Mahila Mahavidyalaya  
Umrer Road, Nagpur-9.

PATENTS ACT 1990







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# CERTIFICATE OF GRANT INNOVATION PATENT

**Patent number:** 2021106725

The Commissioner of Patents has granted the above patent on 24 November 2021, and certifies that the below particulars have been registered in the Register of Patents.

**Name and address of patentee(s):**

Chaitali Mehare of Department of Physics, R.T.M. Nagpur University Nagpur 440033 India

Renu Nayar of Department of Chemistry, D.P. Vipra College Bilaspur India

Sushama Kulkarni of Department of Electronic Science, M.S.G. College Malegaon Camp 423105 India

Vaishali Salunke of Department of Electronic Science, M.S.G. College Malegaon Camp 423105 India

Nirupama Dhoble of Department of Chemistry, Sevadal Mahila Mahavidhyalaya Nagpur 440009 India

Sanjay Dhoble of Department of Physics, R.T.M. Nagpur University Nagpur 440033 India

**Title of invention:**

A synthesis of  $\text{CaAl}_2\text{Si}_4\text{O}_{12}:\text{Dy}^{3+}$  blue phosphor for LED application

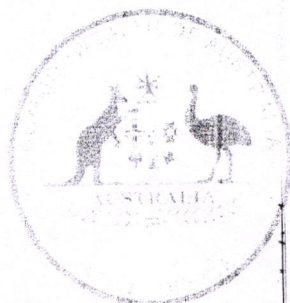
**Name of inventor(s):**

Mehare, Chaitali; Nayar, Renu; Kulkarni, Sushama; Salunke, Vaishali; Dhoble, Nirupama and Dhoble, Sanjay

**Term of Patent:**

Eight years from 24 August 2021

NOTE: This Innovation Patent cannot be enforced unless and until it has been examined by the Commissioner of Patents and a Certificate of Examination has been issued. See sections 120(1A) and 129A of the Patents Act 1990, set out on the reverse of this document.



  
Dated this 24<sup>th</sup> day of November 2021  
Principal  
Sevadal Mahila Mahavidyalaya  
Umber Road, Nagpur-9  
Commissioner of Patents

PATENTS ACT 1990





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GOVERNMENT OF INDIA  
पेटेंट कार्यालय  
THE PATENT OFFICE  
पेटेंट प्रमाणपत्र  
PATENT CERTIFICATE  
(Rule 74 Of The Patents Rules)

क्रमांक : 022114869  
SL No :



पेटेंट सं. / Patent No. : 377219  
आवेदन सं. / Application No. : 201921036337  
फाइल करने की तारीख / Date of Filing : 10/09/2019  
पेटेटी / Patentee : 1.Chaitali M. Mehare 2.Yatish R. Parauha 3.Manohar D.Mehare 4.N.S. Dhoble et al.

प्रमाणित किया जाता है कि पेटेटी को उपरोक्त आवेदन में यथाप्रकटित PROCESS FOR SYNTHESIS OF EU2+ ACTIVATED K6CA4(SO4)6F2 DOWN-CONVERSION PHOSPHOR FOR WHITE LIGHT EMITTING DIODES नामक आविष्कार के लिए, पेटेंट अधिनियम, १९७० के उपबंधों के अनुसार आज तारीख 10th day of September 2019 से बीस वर्ष की अवधि के लिए पेटेंट अनुदत्त किया गया है।

It is hereby certified that a patent has been granted to the patentee for an invention entitled PROCESS FOR SYNTHESIS OF EU2+ ACTIVATED K6CA4(SO4)6F2 DOWN-CONVERSION PHOSPHOR FOR WHITE LIGHT EMITTING DIODES as disclosed in the above mentioned application for the term of 20 years from the 10th day of September 2019 in accordance with the provisions of the Patents Act, 1970.



अनुदान की तारीख : 17/09/2021  
Date of Grant :



Principal  
पेटेंट नियंत्रक  
Controller of Patent

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, 10th day of September 2021 को और उसके पश्चात् प्रत्येक वर्ष में उसी दिन देय होगी।  
Note. - The fees for renewal of this patent, if it is to be maintained will fall / has fallen due on 10th day of September 2021 and on the same day in every year thereafter.



(12) PATENT APPLICATION PUBLICATION

(21) Application No.201921036337 A

(19) INDIA

(22) Date of filing of Application :10/09/2019

(43) Publication Date : 25/10/2019

(54) Title of the invention : PROCESS FOR SYNTHESIS OF EU2+ ACTIVATED K6CA4(SO4)6F2 DOWN-CONVERSION PHOSPHOR FOR WHITE LIGHT EMITTING DIODES

(51) International classification	:G02B11/16	(71)Name of Applicant :
(31) Priority Document No	:NA	1)Chaitali M. Mehare
(32) Priority Date	:NA	Address of Applicant :Department of Physics, R.T.M. Nagpur
(33) Name of priority country	:NA	University, Nagpur-440033 Maharashtra India
(86) International Application No	:NA	2)Yatish R. Parauha
Filing Date	:NA	3)Manohar D.Mehare
(87) International Publication No	:NA	4)N.S. Dhoble
(61) Patent of Addition to Application Number	:NA	5)Sanjay J. Dhoble
Filing Date	:NA	(72)Name of Inventor :
(62) Divisional to Application Number	:NA	1)Chaitali M. Mehare
Filing Date	:NA	2)Yatish R. Parauha
		3)Manohar D.Mehare
		4)N.S. Dhoble
		5)Sanjay J. Dhoble

(57) Abstract :

The present invention relates to a process for synthesis of Eu2+ activated K6Ca4(SO4)6F2 down-conversion phosphor white light emitting diodes. The proposed K6Ca4 (SO4)6F2: xmol%Eu2+(x= 0.5, 2.0, 3.0, 5.0, 7.0, 10.0mol %) phosphor are synthesized via two step solid state diffusion method at high temperature (800oC).Pure crystalline formation, morphological behaviour of synthesized Eu2+ activated K6Ca4(SO4)6F2 phosphor is verified by the X-ray diffraction, Scanning Electron Microscopy. The photoluminescence spectrum and CIE coordinate with color purity also characterized. In PL emission spectra PL excitation spectra observe at 326nm but some part of these spectra lies to 350nm to 400nm. This is useful for generation of white light because it may be used as near UV light. Following invention is described in detail with the help of Figure 1 of sheet 1 showing XRD pattern of Eu2+ doped K6Ca4(SO4)6F2 phosphor.

No. of Pages : 20 No. of Claims : 1

The Patent Office Journal No. 43/2019 Dated 25/10/2019



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**Dr. S. J. Dhoble**

**Professor**

**CERTIFICATE**

**Outward no.** 55D/phys/2020/041

**Date:** 28-08-2020

This is certify that Dr (Mrs.) N. S. Dhoble, Associate Professor in Chemistry, Sevadal Mahila Mahavidyalaya, Nagpur, had been associated in research work that has resulted into following patents titled:

**Title of Published patents:**

Method for the synthesis of degradable black pepper composite material, Archana S. Deshpande, Yatish R. Parauha, Sarang J. Deshpande, **Nirupama S. Dhoble** and Sanjay J. Dhoble, **Indian Patent, Published, Patent number** : 201921020429 A, Date of Granted patent : 25-10-2019.

Automatic microcontroller based ice defrosting instrument, Sanjay. J. Dhoble, Govind B. Nair, Vibha. Chopra, Anup P. Bhat and **Nirupama. S. Dhoble**, **Indian Patent, Published, Patent number** : 201921029249 A, Date of Granted patent : 25-10-2019.

An ultra violet sanitizer for PPE kits, police uniform and clothes, Vibha Chopra, Nutan S. Satpute, **Nirupama S. Dhoble** and Sanjay J. Dhoble, **Indian Patent, Published, Patent number** : 202011020691 A. Date of Granted patent : 26-06-2020.

A process for synthesis of dehydrated luminescent chabazite phosphor, Abhilasha Jain, Chaitali M. Mehare, Neelu Singh, **Nirupama S. Dhoble**, Sanjay J. Dhoble, **Indian Patent, Published, Patent number** : 202021034712 A, Date of Granted patent : 28/08/2020.

  
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**Dr. S. J. Dhoble**  
**Professor**

**CERTIFICATE**

**Outward no.** *SJD/Phy5/2021/071*

**Date:** 24-11-2021

This is certify that Dr (Mrs.) N. S. Dhoble, Professor in Chemistry, Sevadal Mahila Mahavidyalaya, Nagpur, had been associated in research work that has resulted into following patents titled:

**Title of Granted patents:**

A solar cell efficiency enhancement by downshifting layer of  $KALF_4:Dy^{3+}$ ,  $Eu^{3+}$  co-activated downconversion phosphor as spectral converters, Abhijeet R. Kadam, Digambar A. Ovhal, **Nirupama S.Dhoble** and Sanjay J. Dhoble, **Australian Patent, Granted, Patent number : 2021102696, Date of Granted patent : 23-06-2021.**

A low-cost blue-emitting  $Eu^{2+}$  - activated phosphor for NUV excited WLEDs and solar cell applications, Yatish R. Parauha, Sonal P Tatte, **Nirupama S. Dhoble** and Sanjay J. Dhoble, **Australian Patent, Granted, Patent number : 2021102697, Date of Granted patent : 23-06-2021.**

Process for synthesis of  $Eu^{2+}$  activated  $K_6Ca_4(SO_4)_6F_2$  down-conversion phosphor for white light emitting diodes, Chaitali M.Mehare, Yatish R. Parauha, Manohar D.Mehare, **N.S.Dhoble** and Sanjay. J. Dhoble, **Indian Patent, Granted, Patent number : 377219, Date of Granted patent : 17/09/2021.**

A synthesis of  $CaAl_2Si_4O_{12}:Dy^{3+}$  blue phosphor for LED application, Chaitali M. Mehare, Renu Nayar, Sushama C. Kulkarni, Vaishali T. Salunke, **Nirupama S. Dhoble** and Sanjay J. Dhoble, **Australian Patent, Granted, Patent number : 2021106725, Date of Granted patent : 24-11-2021.**



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